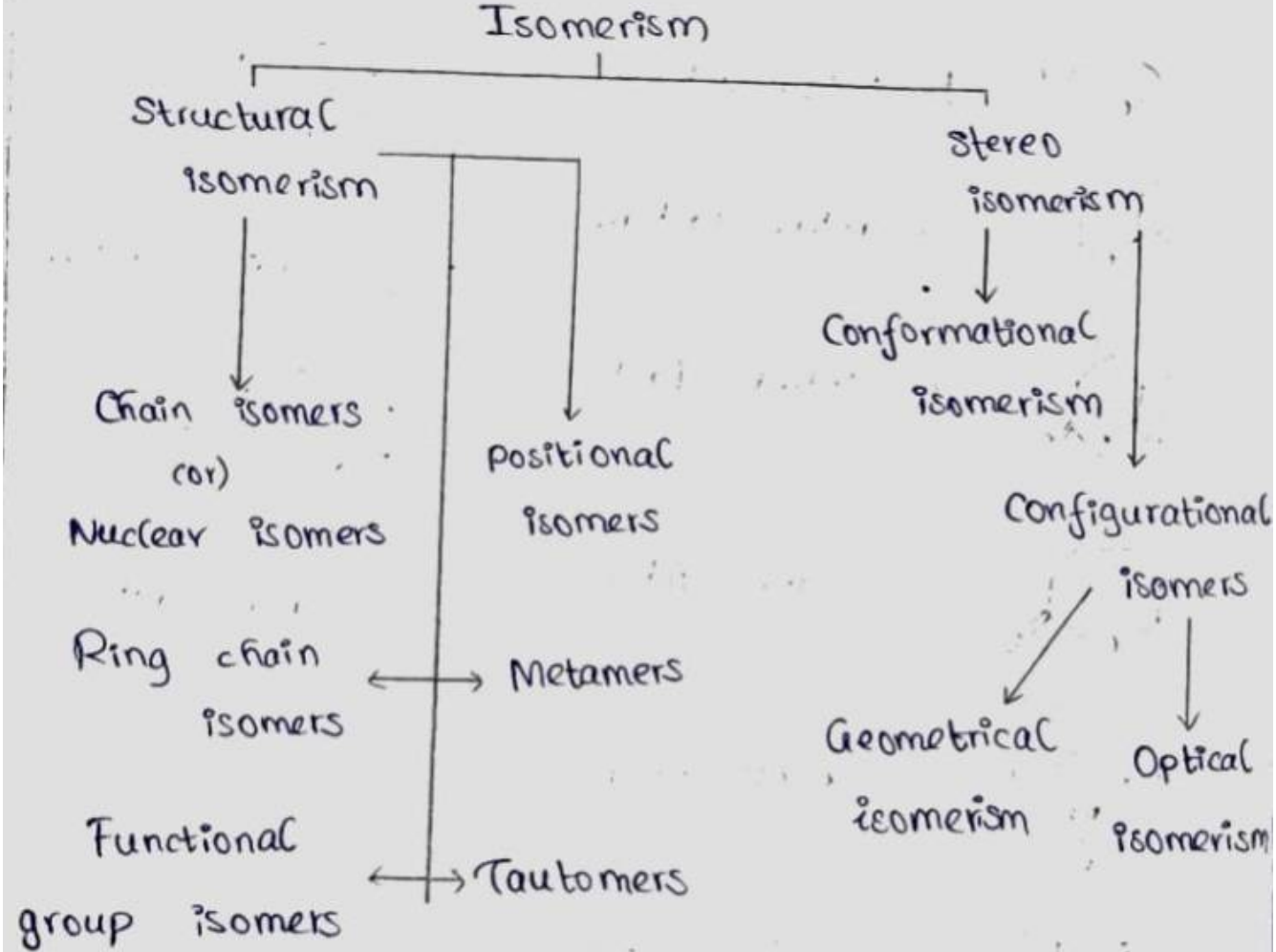
Isomerism

Organic compounds having same molecular formula but different physical and chemical properties or at least physical properties are called as isomers and the phenomenon is called isomerism.

It is divided into two types:

(i) Structural isomerism / Constitutional isomerism

(ii) Stereo isomerism / space isomerism



Chain isomerism / Nuclear isomerism:

Isomers having same Molecular Formula but different length of carbon chain are called as chain isomers.

*) **In alkanes:**

C_4H_{10} (Butane)

$CH_3 - CH_2 - CH_2 - CH_3$

n-Butane

$CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_3$

Isobutane/

2-methyl propane

C_5H_{12} (pentane)

$CH_3 - CH_2 - CH_2 - CH_2 - CH_3$

n-pentane

$CH_3 - CH_2 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_3$ (or) $CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2 - CH_3$

Isopentane/

2-methyl butane

$CH_3 - \underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}} - CH_3$ (neopentane)

Min. number of carbon atoms required for an "alkane" to show isomerism is "4".

Alkane	Isomers
CH_4	-
C_2H_6	-
C_3H_8	-
C_4H_{10}	2

C_5H_{12}	3
C_6H_{14}	5
C_7H_{16}	9
C_8H_{18}	18
C_9H_{20}	35
$C_{10}H_{22}$	75

*) In alkenes:

C_4H_8 (Butene)

$CH_2^{1} = CH^{2} - CH_2^{3} - CH_3^{4}$

1-Butene

$CH_2^{1} = C^{2}(CH_3) - CH_3^{3}$

Iso butene / 2-Methyl Propene

Min. number of carbon atoms required for an "alkene" to show chain isomerism is 4.

*) In alkynes:

C_5H_8 C_4H_6 $CH \equiv C - CH_2 - CH_3$ (X)

(Butyne)

(Min. no. of carbon atoms required for an "alkyne" to show chain isomerism is 5).

C_5H_8 (Pentyne)

$CH \equiv C - CH_2 - CH_2 - CH_3$

(n-pentyne)

(1-pentyne)

$CH \equiv C - CH(CH_3) - CH_3$

(Isopentyne)

Positional Isomers:

Isomers having same MF but different position of double bond / triple bond / functional group / substituent is are known as positional isomers.

Alkane - 6 carbon atoms are required (Min.)

*) In alkene :

(Min. no. of carbon atoms required for an "alkene" to show positional isomerism is 4.)

C_4H_8 (Butene)

$CH_2 = CH - CH_2 - CH_3$ (1-Butene)

$CH_3 - CH = CH - CH_3$ (2-Butene)

*) In alkyne :

C_4H_6 (Butyne)

$HC \equiv C - CH_2 - CH_3$ (1-Butyne)

$CH_3 - C \equiv C - CH_3$ (2-Butyne)

(Min. no of carbon atoms req. for an "alkyne" to show Positional isomerism is 4.)

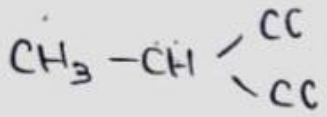
*) In alkyl halides (R-X):

① $CH_3CH_2CH_2Cl$ (n-propyl chloride) (1-chloro propane) (C_3H_7Cl)

$CH_3 - \underset{Cl}{\underset{|}{CH}} - CH_3$ (OR) Isopropyl chloride (or) 2-chloro propane

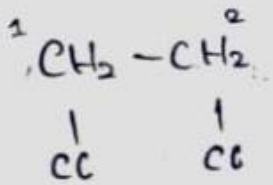
$(CH_3)_2CHCl$

② $C_2H_4Cl_2$



1,1 - dichloro ethane

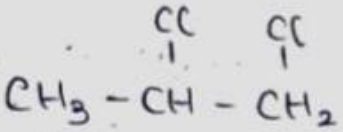
(ethylidene chloride)



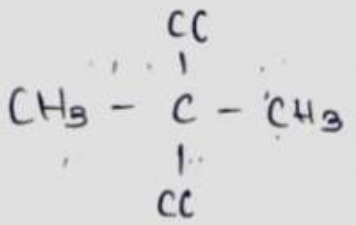
(1,2 - dichloro ethane)

(ethylene chloride)

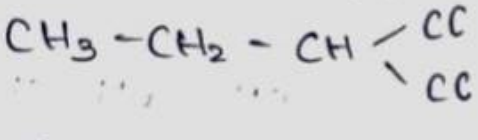
③ $C_3H_6Cl_2$



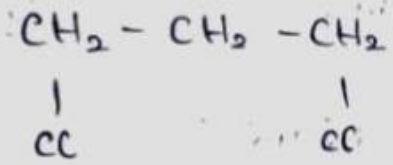
(1,2 - dichloro propane)



(2,2 - dichloro propane)



(1,1 - dichloro propane)



(1,3 - dichloro propane)

*) In alcohols:

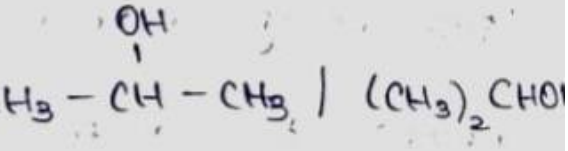
General formula (ROH)

① $CH_3-CH_2-CH_2-OH$

n-propyl alcohol

(1-propanol)

(C_3H_8O)



2-propanol | Isopropyl alcohol

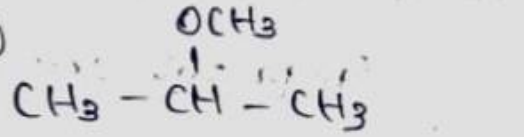
*) In ethers: (R-O-R)

① $CH_3-CH_2-CH_2-O-CH_3$

propyl methyl ether

(1-methoxy propane)

$(C_4H_{10}O)$



Isopropyl methyl ether

(2-methoxy propane)

*) In Ketones: ($R-\overset{O}{\overset{\|}{C}}-R$)

($C_5H_{10}O$)

$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_3$ 2-pentanone

$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$ 3-pentanone

Butyl chloride:

MF: C_4H_9Cl

(I) $CH_3-CH_2-CH_2-CH_2-Cl$

(II) $CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{CH}}-CH_2-Cl$

(III) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3\ Cl$

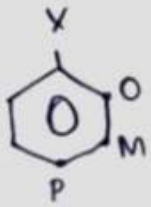
(IV) $CH_3-CH_2-\underset{\underset{Cl}{|}}{CH}-CH_3$

I & II - Chain isomers ; I & III - Chain and positional isomers

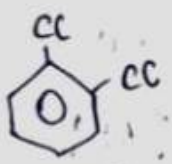
I & IV - Positional isomers

II & III - Positional isomers ; III & IV - Chain isomers

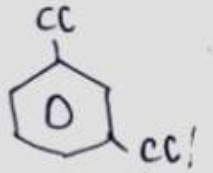
Benzene:



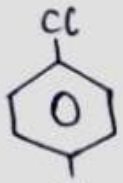
MF: $C_6H_4Cl_2$



(1,2)

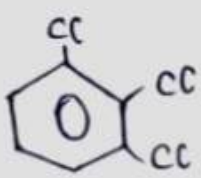


(1,3)

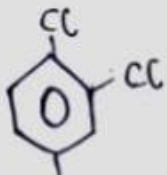


(1,4)

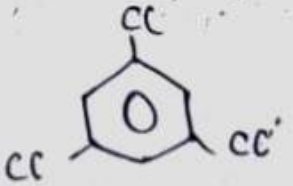
MF: $C_6H_3Cl_3$



(1,2,3)

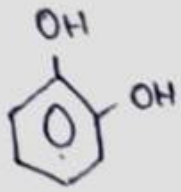


(1,2,4)



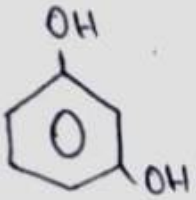
(1,3,5)

MF: $C_6H_6O_2$



(1,2)

(Catechol)



(1,3)

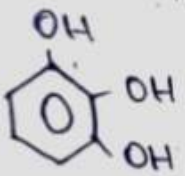
(Resorcinol)

(1,4)

Hydroquinone/

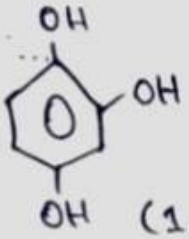
p-quinol

MF: $C_6H_6O_3$



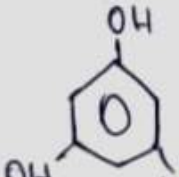
(1,2,3)

Pyrogallol



(1,2,4)

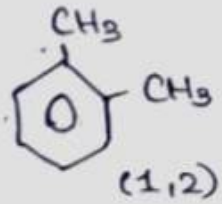
Hydroxy quinol



(1,3,5)

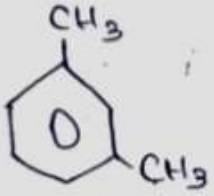
Phloroglucene

MF: C_8H_{10}



(1,2)

O-xylene



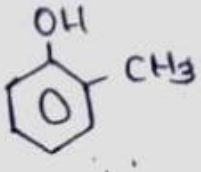
(1,3)

m-xylene

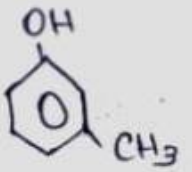
(1,4)

p-xylene

MF: C_7H_8O



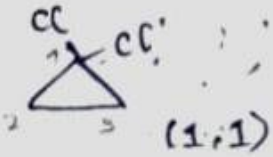
o-cresol



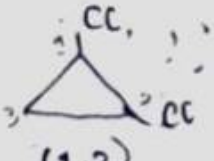
m-cresol

p-cresol

MF: $C_3H_4Cl_2$ (cyclic)

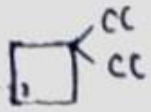


(1,1)

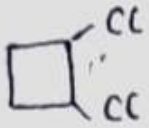


(1,2)

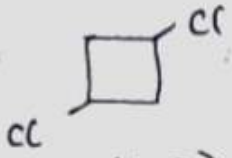
MF: $C_4H_6Cl_2$ (cyclic)



(1,1)



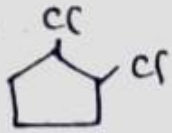
(1,2)



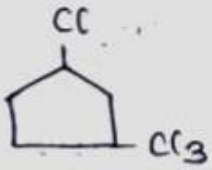
(1,3)

MF: $C_5H_8Cl_2$ (cyclic)

(1,1)

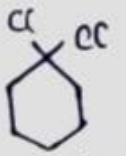


(1,2)

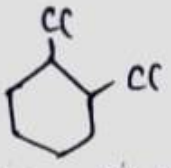


(1,3)

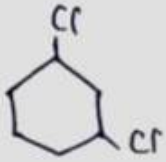
MF: $C_6H_{10}Cl_2$ (cyclic)



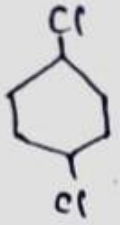
(1,1)



(1,2)



(1,3)



(1,4)

Ring chain isomerism:

Isomers having same MF, one isomer is in chain form and other one is in ring form are called as ring-chain isomers. These are one type of functional group isomers.

① Alkenes | Cyclo alkanes

MF: C_3H_6 $CH_2 = CH - CH_3$ | $\triangle$

DBE = 1°

MF: C_4H_8 $CH_2 = CH - CH_2 - CH_3$ $\square$

DBE = 1° $CH_3 - CH = CH - CH_3$ $\triangle$

(2) Alkyne, alkadiene, cyclo alkene

MF: C_3H_4 $CH_3-C\equiv CH$ | $CH_2=C=CH_2$ |

DBE = 2°

MF: C_4H_6 DBE = 2° $HC\equiv C-CH_2-CH_3$

$CH_3-C\equiv C-CH_3$ $CH_2=C=CH-CH_3$

$CH_2=CH-CH=CH_2$

Metamerism:

Isomers having same functional group attached to different alkyl groups called as metamers.

In ~~alcohols~~ ethers: (R-O-R)

MF: $C_4H_{10}O$ $CH_3-CH_2-O-CH_2-CH_3$ (I)

$CH_3-O-CH_2-CH_2-CH_3$ (II)

$CH_3-O-CH(CH_3)(CH_3)$ (III)

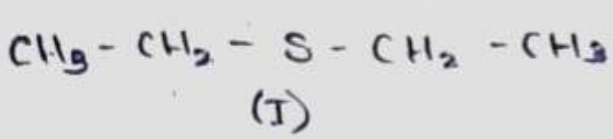
I & II : Metamers

I & III : Metamers

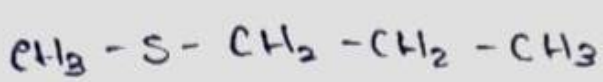
II & III : Positional isomers

In thio ethers: (R-S-R)

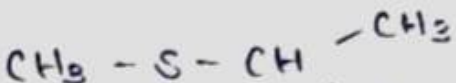
MF: $C_4H_{10}S$



(I)



(II)

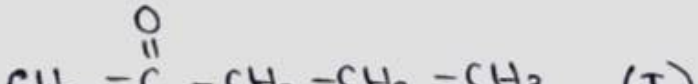


(III)

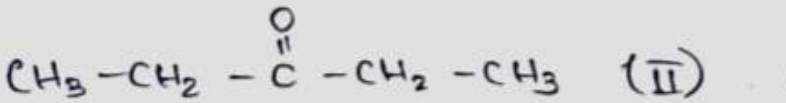
I & II → Metamers I & III → Metamers

II & III → Positional isomers

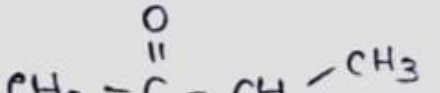
In Ketones : (R–C(=O)–R)



(I)



(II)

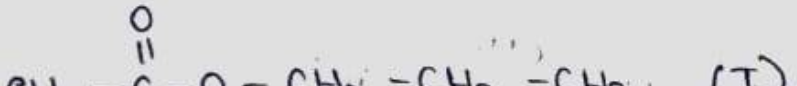


(III)

I & II → Metamers | Positional isomers

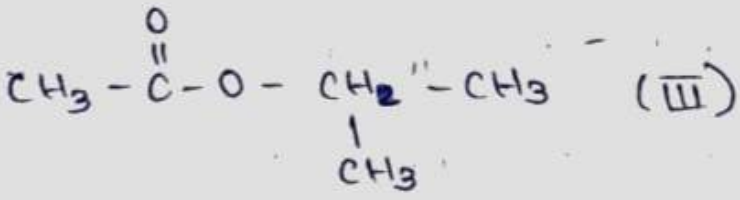
I & III → Metamers ∴ II & III → Metamers

In esters : (R–C(=O)–O–R)



(I)

(II)

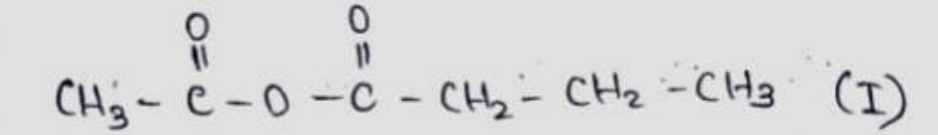


(III)

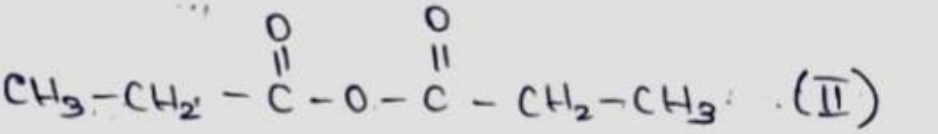
I & II → Metamers II & III → Metamers

I & III → Metamers

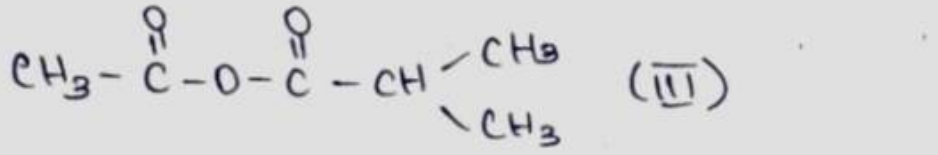
In anhydrides : $(RCO)_2O$ $\left(-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-\right)$



(I)



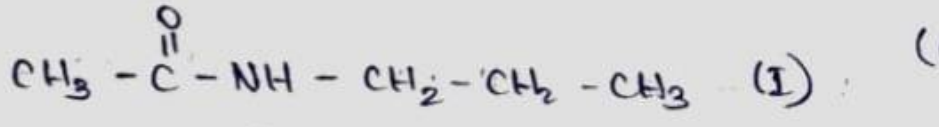
(II)



(III)

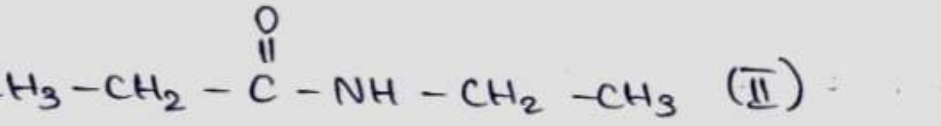
I & II
II & III
I & III
→ Metamers

In N-acyl amides : $R-\overset{O}{\overset{\|}{C}}-NH-R$

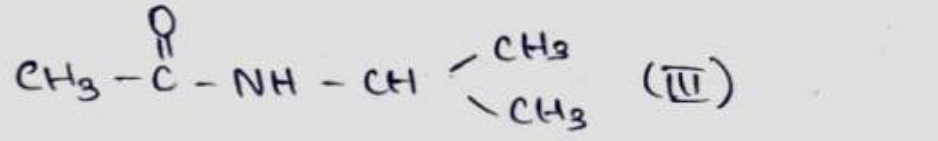


$(C_5H_{11}NO)$

(I)



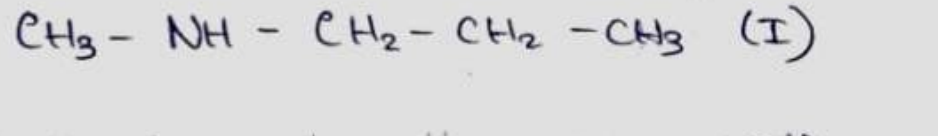
(II)



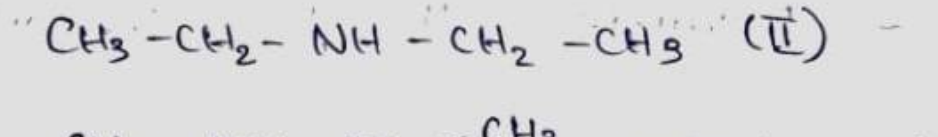
(III)

[I & II ; II & III ; I & III] → Metamers

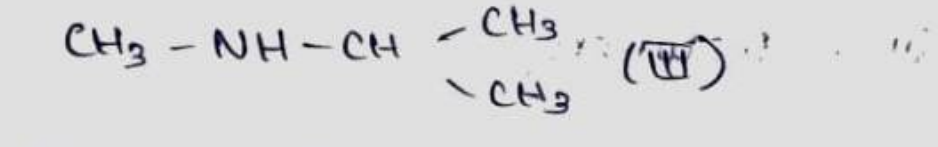
In 2° amines (R_2NH): $(C_4H_{11}N)$



(I)



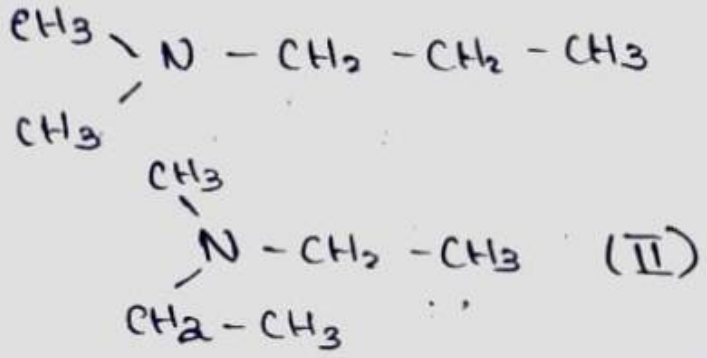
(II)



(III)

[I & II ; II & III ; I & III] → Metamers

In 3° Amines : (R_3N)



(I)

(II)

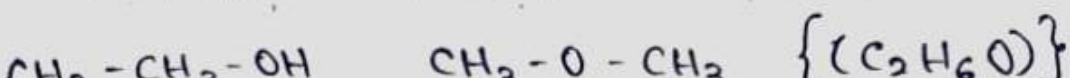
I & II - metamers

Functional group isomerism :

Isomers having same MF but attached to different functional groups are called as functional group isomers.

① Alcohols & Ethers :

(R-OH) (R-O-R)

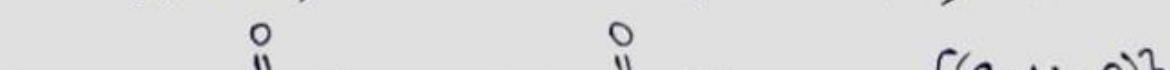


{(C_2H_6O)}

(Ethanol) (Methoxy methane)

② Aldehydes & Ketones :

(R-CHO) ~~(R-COOR)~~ (R-C(=O)-R)

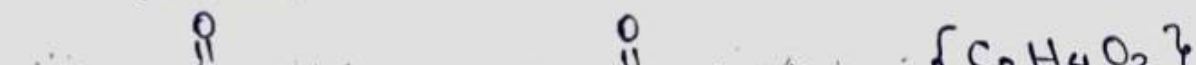


{(C_3H_6O)}

(propanal) (propanone)

③ Carboxylic acid & Esters :

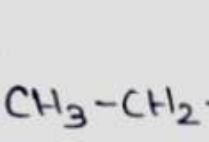
(RCOOH) (RCOOR)

i) 

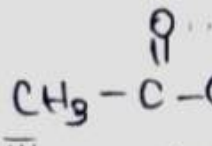
{$C_2H_4O_2$}

(Ethanoic acid) (Methyl methanoate)

ii)



(I)



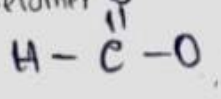
(II)

I & II → FG

I & III → FG

II & III → Metamer (OR)

$\{C_3H_6O_2\}$



(III)

④ Alkyl cyanides & isocyanides:

(RCN) (RNC)

[Except HCN & HNC]

(i) CH_3CN CH_3NC $[C_2H_3N]$

(Ethane nitrile) (Methyl carbylamine)

(Methyl iso nitrile)

(Methyl iso cyanide)

(ii) CH_3CH_2CN CH_3CH_2NC $\{C_3H_5N\}$

(Ethyl cyanide) (Ethyl iso cyanide)

⑤ Nitro alkanes & alkyl nitrites:

$(R-NO_2)$ $(R-ONO)$

$CH_3-CH_2-NO_2$ CH_3-CH_2-ONO $\{C_2H_5NO\}$

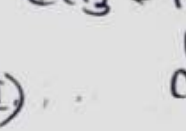
⑥ 1°, 2° & 3° Amines:

$(R-NH_2)$ (R_2NH) (R_3N)

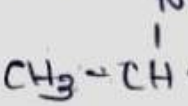
$CH_3CH_2CH_2NH_2$ $CH_3-NH-CH_2-CH_3$ (III)

(I)

$\{C_3H_9N\}$



(IV)



(II)

(7) Amides, oximes and nitroso compounds:

(D - C(=O)NH2) (D - CH = N - OH) (D - NO)

CH3 - CH2 - C(=O) - NH2 CH3 - CH2 - CH = N - OH

CH3 - CH2 - CH2 - NO {C3H7NO}

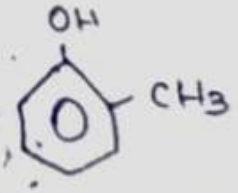
(8) Benzyl alcohol and phenol derivatives:

i)

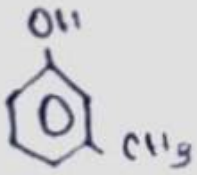
(Benzyl alcohol)

ii)

(Methoxy benzene)
(Anisole)

iii) 

(O-cresol)

iv) 

(m-cresol)

v)

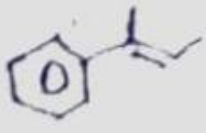
(p-cresol)

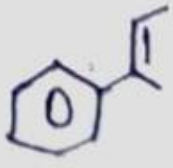
(i), (ii) & (iii) - FG

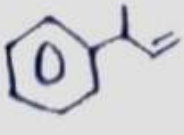
(iii), (iv) & (v) - positional isomers

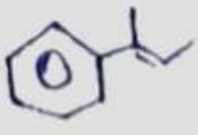
Q) How many are not positional isomers of each other ?

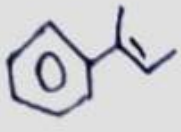
(I)

(II) 

(III) 

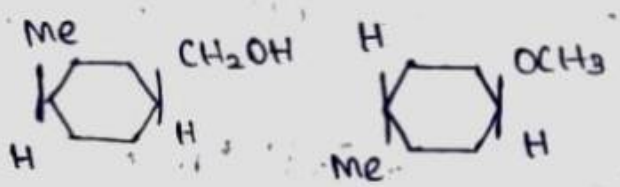
(IV) 

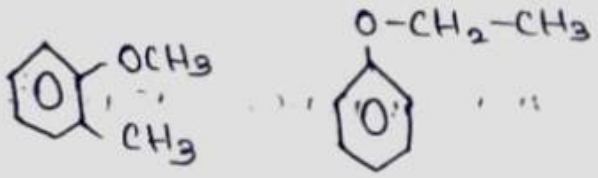
(V) 

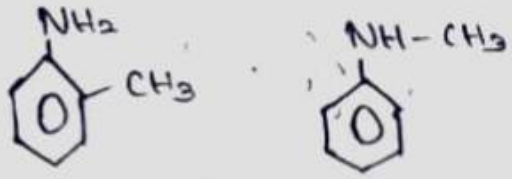
(Farne) 

Q) Functional isomers

(I) (✓)

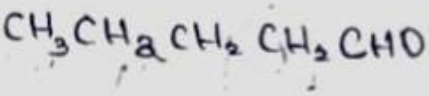
(II)  (✓)

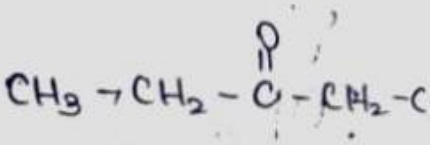
(III)  (✗)

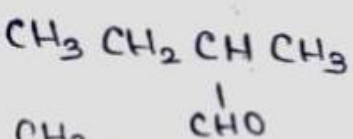
(IV)  (✓)

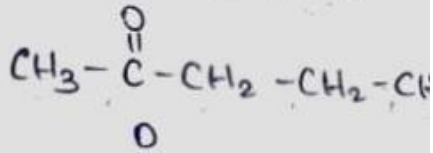
Q) How many structurally isomeric (carbonyl compounds) are possible with MF $C_5H_{10}O$:

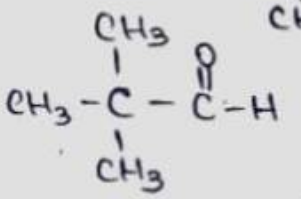
aldehydes & ketones

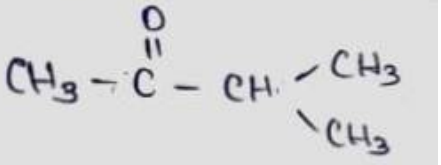


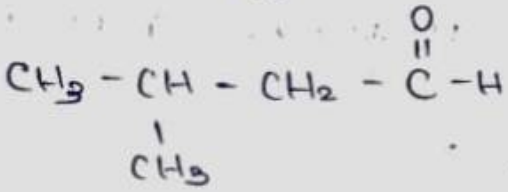












(7)

Stereo isomerism:

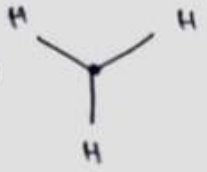
Isomers having same molecular formula but different spatial arrangement of atoms or groups are called as stereo isomers.

Conformational isomers:

Isomers which are obtained by free rotation of atoms / groups WRT C–C are called as conformational isomers. These isomers are observed in alkanes, derivatives of alkanes & higher cyclo alkanes.

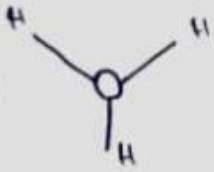
Newman projection:

(OR)

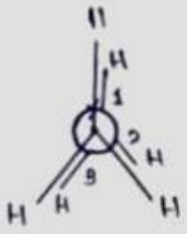


(Front carbon)

(OR)

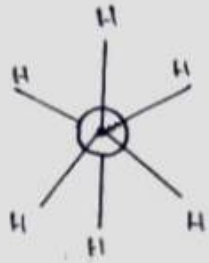


(Back carbon)



Eclipsed (E)

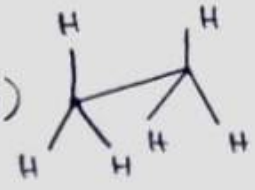
$\overset{60^\circ}{\rightleftharpoons}$



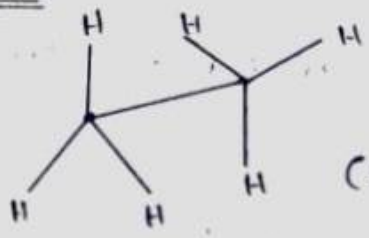
Staggered (S)

$\overset{60^\circ}{\rightleftharpoons}$ E

Sawhorse projection:



(Eclipsed)



(staggered)

Dihedral angle:

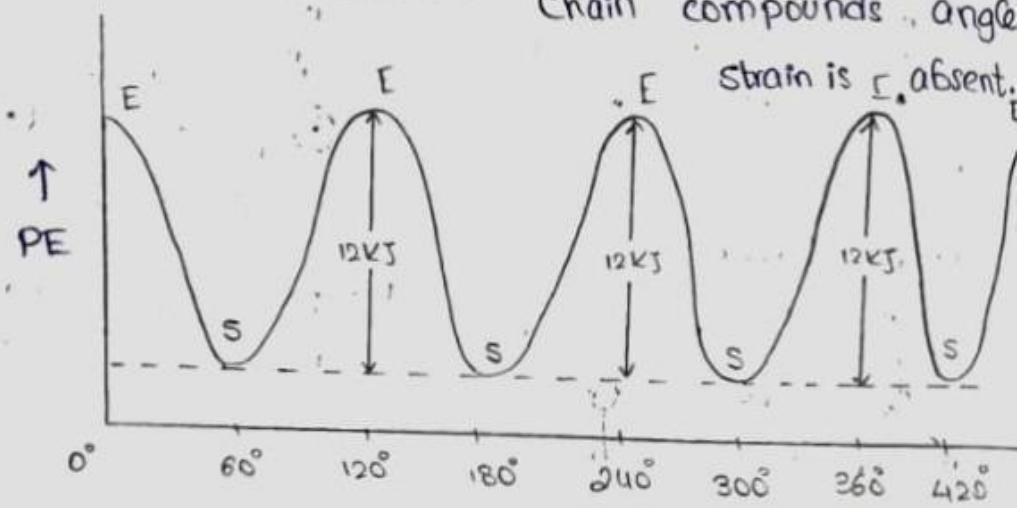
Angle b/w C-H bond of one carbon atom to C-H bond of another carbon atom is called as dihedral angle.

Tortional strain :

Strain, due to repulsions of bonding $e^{\ominus}$ of one substituent to near by substituent is called as tortional strain. It is more in eclipsed form compared to staggered. Therefore staggered form is more stable than eclipsed form.

Energy profile diagram :

Note : In acyclic / open chain compounds angle strain is absent.



Dihedral angle (θ) →

Energy : Eclipsed > staggered

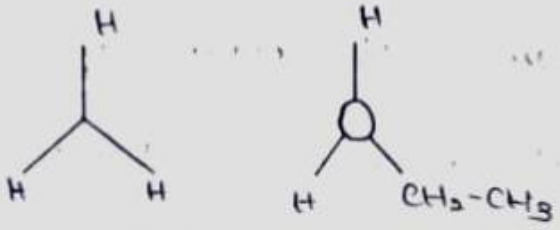
Stability : Eclipsed < staggered

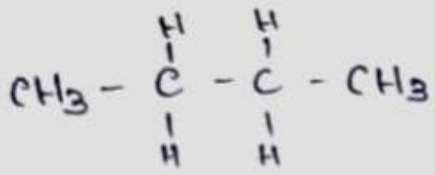
Butane :

MF : C_4H_{10}

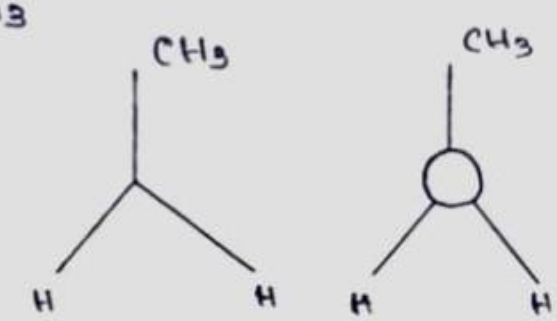
$CH_3-CH_2-CH_2-CH_3$

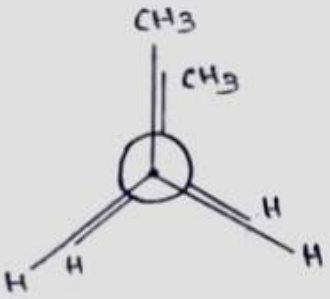
WRT C_1-C_2



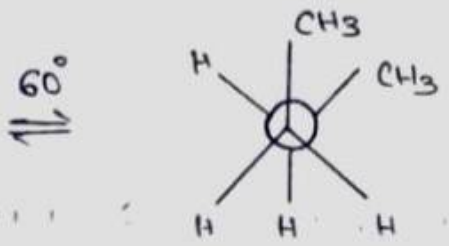


WRT C_2-C_3

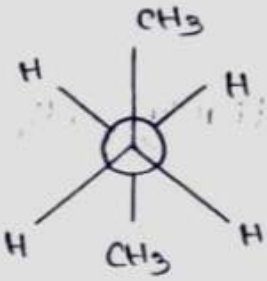




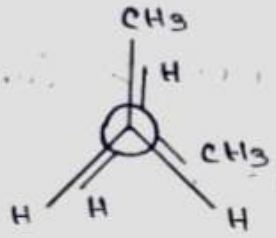
(Fully eclipsed)



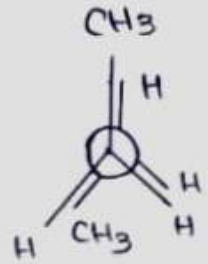
(Gauche / skew form)



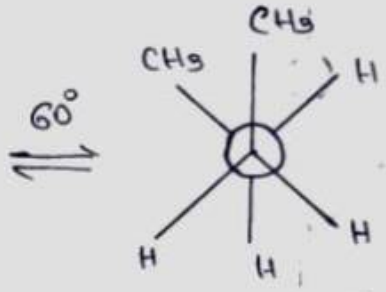
(Anti-form $\mu = 0$)



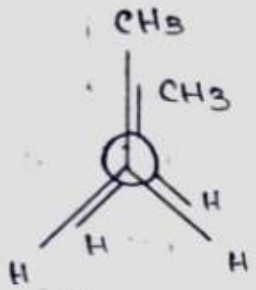
(Partially eclipsed)



(Partially eclipsed)



(Gauche / skew form)



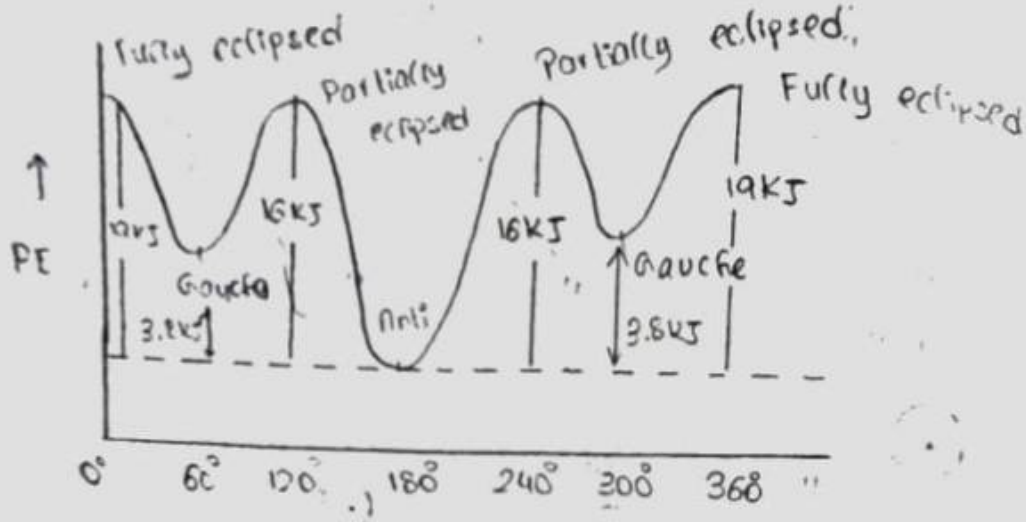
(Fully eclipsed)

Stearic strain :

Strain due to repulsions of bulky atoms / groups when approach together / close together is called as stearic strain.

"Fully eclipsed form" has more stearic strain, so

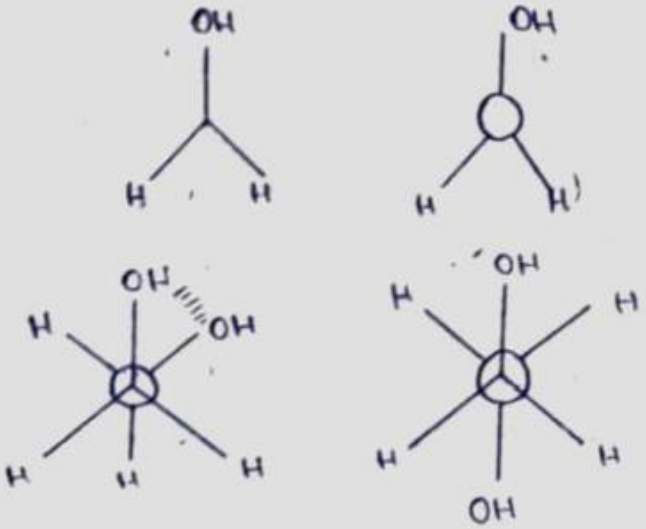
it is unstable.



Energy : Fully eclipsed > Partially eclipsed > Gauche > Anti

Stability : Anti > Gauche > Partially eclipsed > Fully eclipsed

$HO-CH_2-CH_2-OH$ (Ethylene glycol)



Gauche Anti

Stability : Gauche > Anti (Because of hydrogen bond)

$HO-CH_2-CH_2-X$

where X = $-F$; $-NO_2$; $-NH_2$; $-NHR$; $-NR_2$; $-\overset{O}{\overset{\|}{C}}-H$; $-\overset{O}{\overset{\|}{C}}-$; $-\overset{O}{\overset{\|}{C}}-OH$; $-OH$.

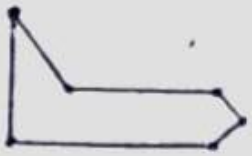
Stability : Gauche > Anti

Cyclo hexane :

Molecular Formula : C_6H_{12}

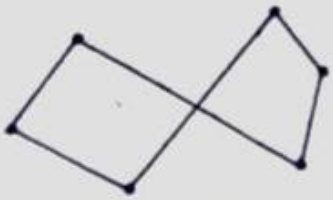
(μ-0) Chair form

⇌ 60°



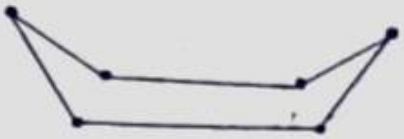
Half chair

⇌ 60°



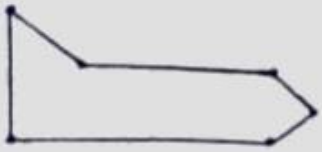
Twist Boat (chiral)

⇌ 60°



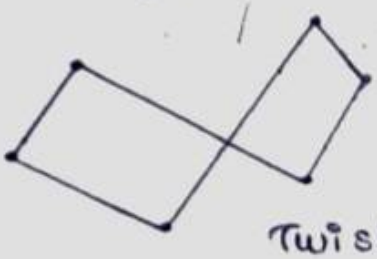
Boat

⇌ 60°



Half chair

⇌ 60°

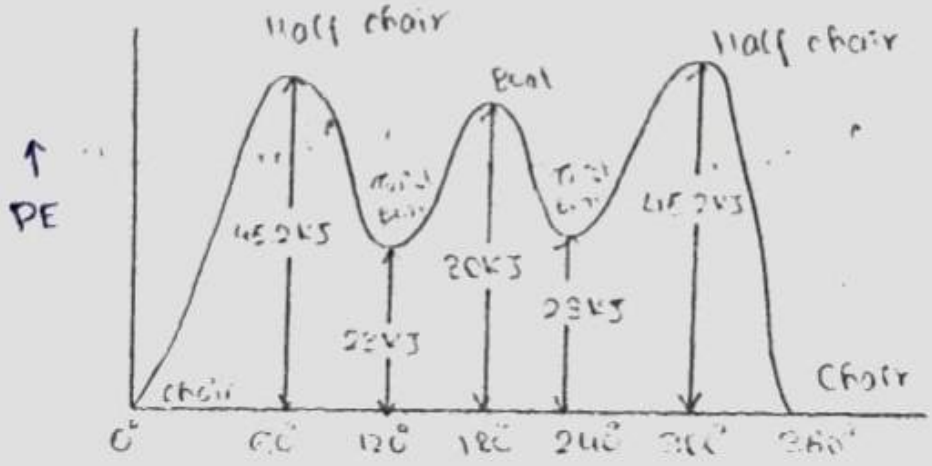


Twist Boat (chiral)

⇌ 60°

chair form (μ-0)

Energy profile :



Energy:

Half chair > Boat > Twist Boat > Chair

Stability:

Chair > Twist Boat > Boat > Half chair

Q) Cyclohexane 1,4-dione is a polar compound having dipole moment value of 1.2D. If mole fraction of its chair form is 0.80 what will be the dipole moment of twisted boat form.

$\mu = 0$

$\mu \neq 0$

$\mu_{net} = \mu_{chair} \times_{chair} + \mu_{twist\ boat} \times_{twist\ boat}$

$1.2 = 0(0.8) + x(0.2)$

$x = 6D$

$\mu_{twist\ boat} = 6D$

Q) μ of a compound $W - CH_2 - CH_2 - W$ is 1.5 debye. If μ of its gauche form is 6 debye what will be the mole fraction of its anti form.

$\mu_{net} = \mu_{Gouche} \times_{Gauche} + \mu_{anti} \times_{anti}$

$1.5\,D = 6\,(x_{Gouche}) + 0$

$x_{Gouche} = \frac{1.5}{6} \Rightarrow 0.25$

$x_{anti} = 1 - 0.25 \Rightarrow 0.75$

Q) How many structural isomers of amines are possible for the MF $C_4H_{11}N$.

i) $CH_3-CH_2-CH_2-CH_2-NH_2$

ii) $CH_3-CH_2-CH_2-NH-CH_3$

iii) $CH_3-CH_2-N(CH_3)-CH_3$

iv) $CH_3-CH(CH_3)-CH_2-NH_2$

v) $CH_3-CH_3-CH(NH_2)-CH_3$

vi) $CH_3-NH-CH(CH_3)_2$

vii) $CH_3CH_2-NH-CH_2CH_3$

viii) $CH_3-C(CH_3)_2-NH_2$

(8)

Q) How many structural isomers are possible by the MF C_4H_9Br

(i) $CH_3-CH_2-CH_2-CH_2-Br$;

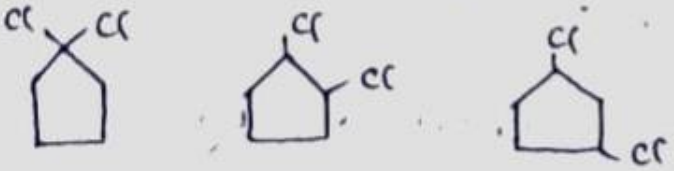
(ii) $CH_3-CH_2-CH(Br)-CH_3$;

(iii) $CH_3-C(CH_3)_2-Br$;

(iv) $CH_3-CH(CH_3)-CH_2-Br$

(4)

Q) How many dichloro derivaties are possible for cyclo pentane & n-butane.



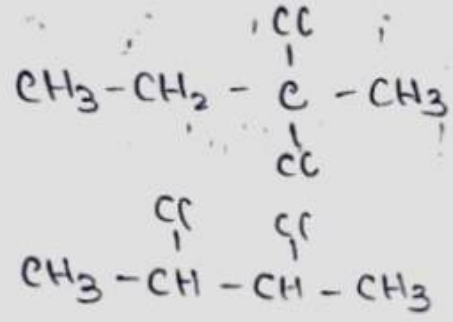
(9)

$CH_3-CH_2-CH_2-CH(Cl)-Cl$

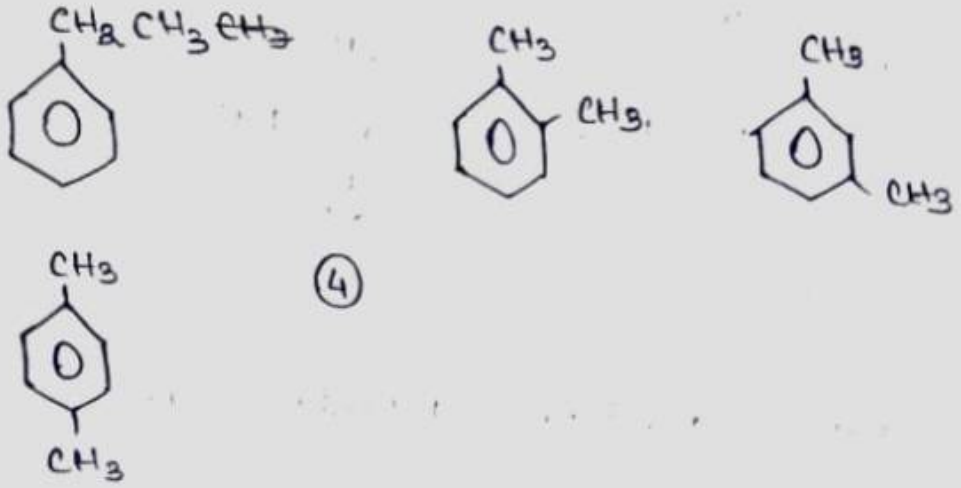
$CH_3-CH(Cl)-CH_2-CH_2-Cl$

$CH_3-CH_2-CH(Cl)-CH_2-Cl$

$Cl-CH_2-CH_2-CH_2-CH_2-Cl$



Q) Write the possible aromatic isomers for MF C_8H_{10}



④

Configurational isomers:

Isomers which are not interconvertable by rotation are called as configurational isomers.

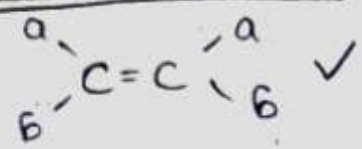
It is of two types:

i) Geometrical ii) Optical

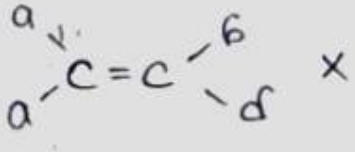
Geometrical isomerism:

Isomers which are obtained by restricted rotation around C=C, C=N, N≡N are called geometrical isomers.

In alkenes:



✓



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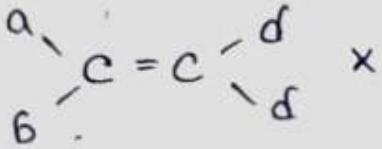

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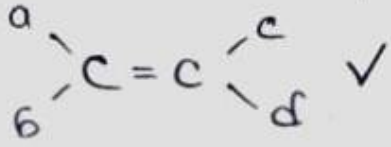
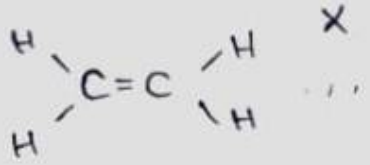


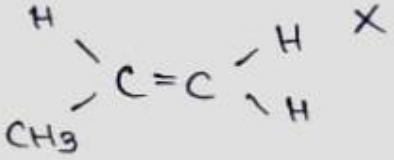
✓

★ $CH_2 = CH_2$



×

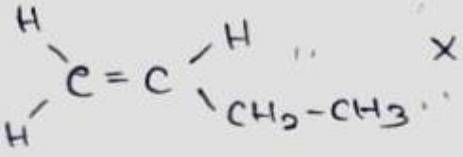
★ $CH_3 - CH = CH_2$



×

★ $CH_2 = CH - CH_2 - CH_3$

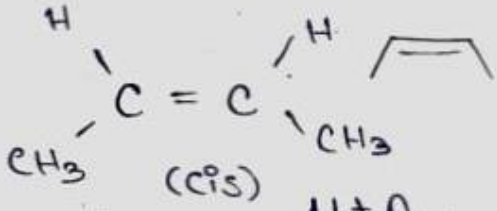
1 - Butene



×

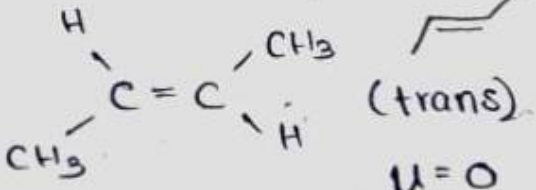
★ $CH_3 - CH = CH - CH_3$

2 - Butene



(cis)

$\mu \neq 0$.

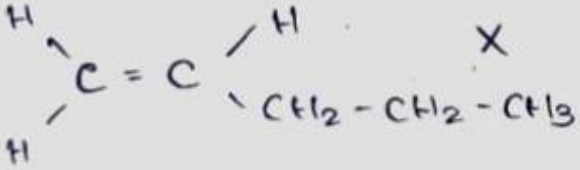


(trans)

$\mu = 0$

★ $CH_2 = CH - CH_2 - CH_2 - CH_3$

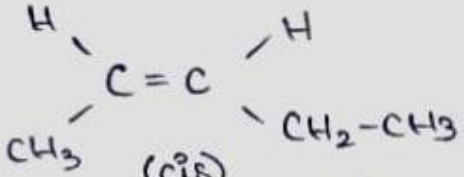
(1 - pentene)



×

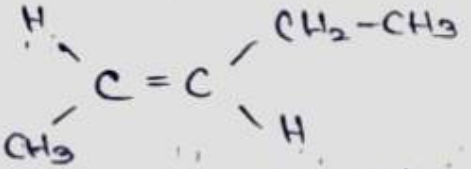
★ $CH_3 - CH = CH - CH_2 - CH_3$

(2 - pentene)



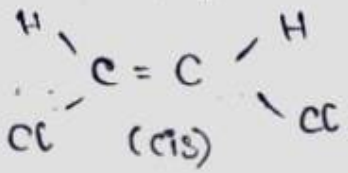
(cis)

$\mu \neq 0$

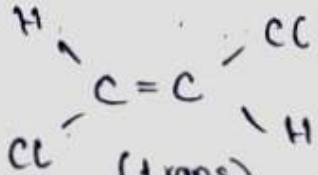


(trans) $\mu \neq 0$

★ $CH_2CC = CHCC$ (1,2 - dichloro ethene)

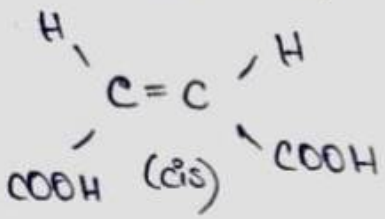


(cis)

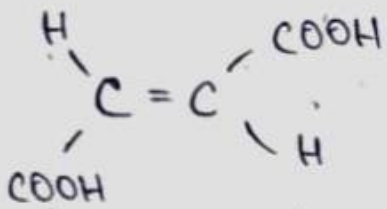


(trans)

★ MF : $C_4H_4O_4$



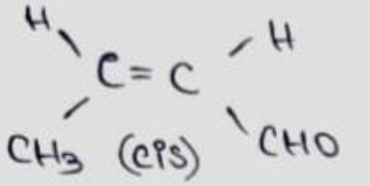
(maleic acid)

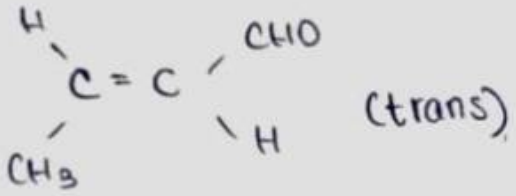


(trans)

(Fumeric acid)

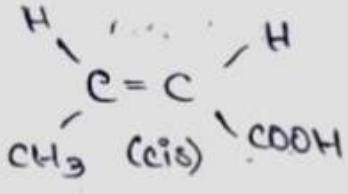
★ $CH_3-CH=CH-CHO$ (Crotonaldehyde)

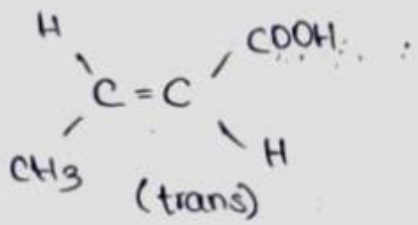




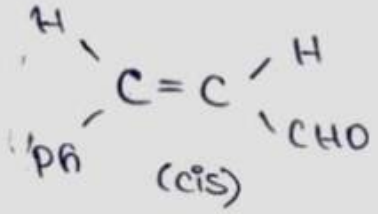
(trans)

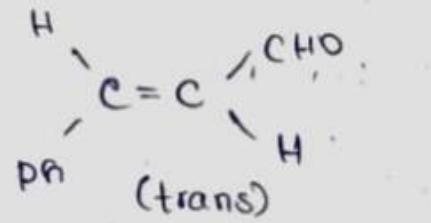
★ $CH_3-CH=CH-COOH$ (crotonic acid)



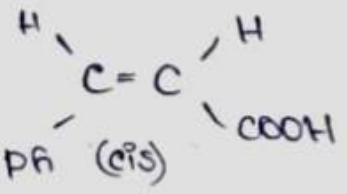


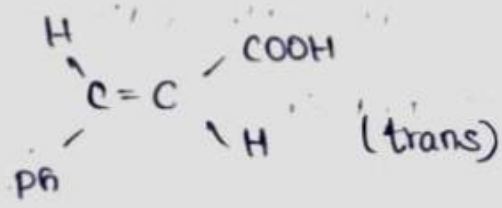
★ $Ph-CH=CH-CHO$ (Cinnamaldehyde)





★ $Ph-CH=CH-COOH$ (cinnamic acid)





★ $CH_2=CH-CH=CH-CH_3$

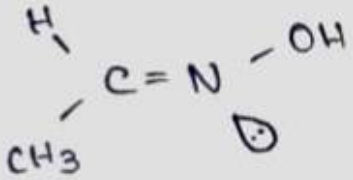
$GI = 2^n = 2^1 = 2$

$-CH=CH-$ is taken as the stereogenic center as it is bonded with different groups / atoms unlike $CH_2=CH-$.

In oximes:

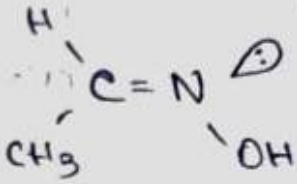
* $R-\underset{\underset{H}{|}}{C}=O + H_2N-OH \xrightarrow[-H_2O]{\Delta} R-CH=\ddot{N}-OH$

(Aldehyde) (Hydroxyl amine) (Aldoxime)



syn-aldoxime

If $R = CH_3$



~~trans~~

anti-aldoxime

$$R-\underset{\underset{R}{|}}{C}=O + H_2N-OH \xrightarrow[-H_2O]{\Delta} R-\underset{\underset{R}{|}}{C}=\ddot{N}-OH$$ ✗

(Ketoxime)

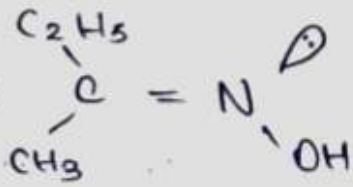
* $R-\underset{\underset{R'}{|}}{C}=O + H_2N-OH \xrightarrow[-H_2O]{\Delta} R-\underset{\underset{R'}{|}}{C}=\ddot{N}-OH$ ✓

(Ketoxime)

If $R = CH_3$, $R' = C_2H_5$

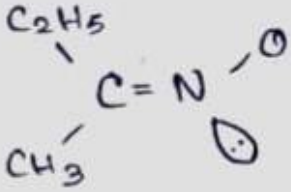
* $CH_3-\underset{\underset{C_2H_5}{|}}{C}=\ddot{N}-OH$

(Ketoxime)



Syn methyl ethyl (OR) ketoxime

Anti ethyl methyl ketoxime

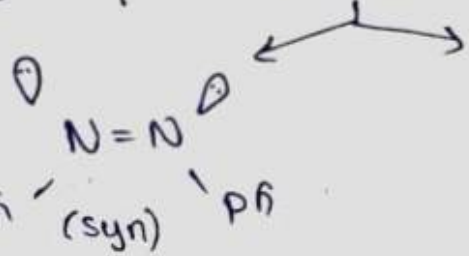


(Syn ethyl methyl ketoxime)

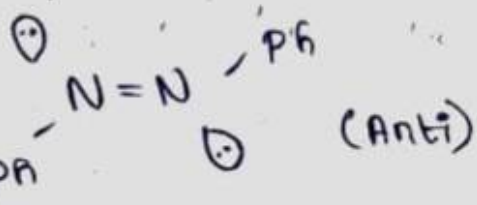
(OR) Anti methyl ethyl ketoxime

In azo compounds:

Eg: $Ph-\ddot{N}=\ddot{N}-Ph$ (Azobenzene)



(syn)



(Anti)

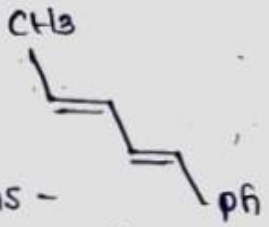
In conjugated dienes:

(1) Having dissimilar ends with even/odd no of double bonds:

$Ph-CH=CH-CH=CH-CH_3$

$G.I = 2^n = 2^2 = 4$

(Cis – Cis)



(Trans – trans)

(Cis-trans)

(Trans – Cis)

(2) Having similar ends with even no. of double bonds:

$CH_3-CH=CH-CH=CH-CH_3$

$G.I = 2^{n-1} + 2^{n/2-1}$

$= 2^{2-1} + 2^{2/2-1} \Rightarrow 2^1 + 2^0$

$\Rightarrow 3$

(3) Having similar ends with odd number of double bonds:

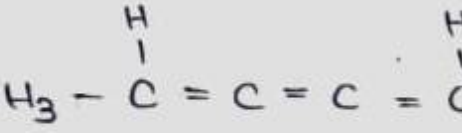
$CH_3-CH=CH-CH=CH-CH=CH-CH_3$

$GI = 2^{n-1} + 2^{\frac{n-1}{2}}$

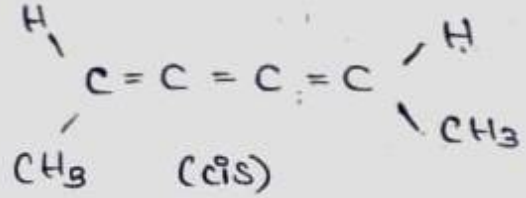
$= 2^{3-1} + 2^{\frac{3-1}{2}} \Rightarrow 2^2 + 2^1 \Rightarrow 6$

In cummulated polyenes:

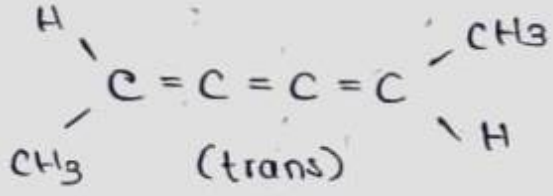
Cummelated polyenes with odd no. of double bonds can show geometrical isomerism



★ $CH_3-CH=C=C=C=CH-CH_3$ ✓



(cis)



(trans)

★ $CH_3-CH=C=C=C=C=CH-CH_3$ ✓

★ $CH_3-CH=C=CH-CH_3$ ✗

even number of double bonds

Optical isomerism ✓ Geometrical isomerism ✗

★ In spiro compounds:

G.I ✓

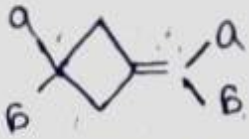
cis trans

↘ odd no. of rings

G.I ✗

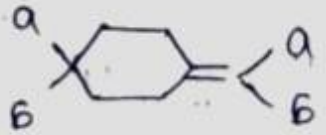
↘ Even no. of rings

In cyclo alkylidenes:



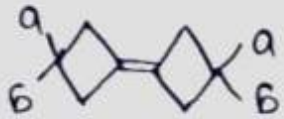
G.I ✓

(cis / trans)



G.I ✓

(cis / trans)



G.I ✓

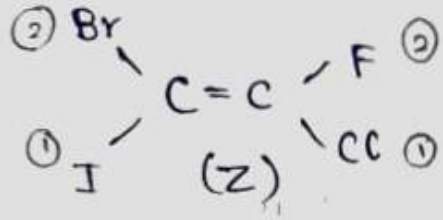
(cis / trans)

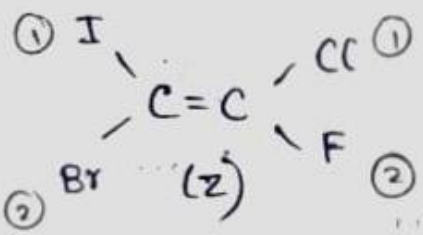
E-Z nomenclature: (one type of geometrical isomers)

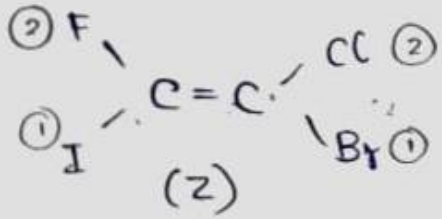
E = Entgagan (opposite)

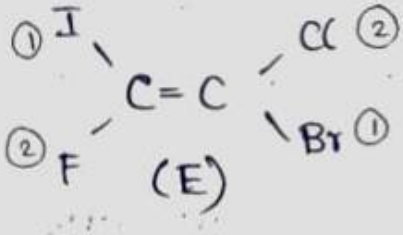
Z = Zusaman (Together)

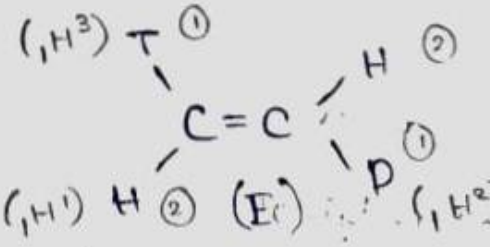
CIP rules (Cohn- Ingold - Prelog rules):

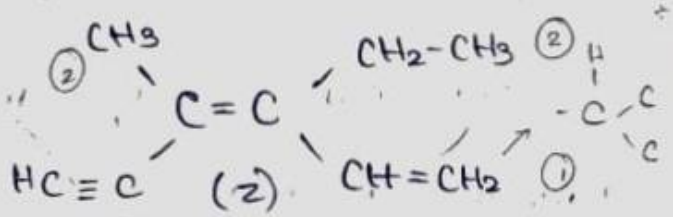


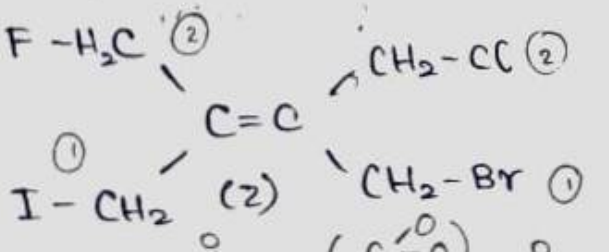


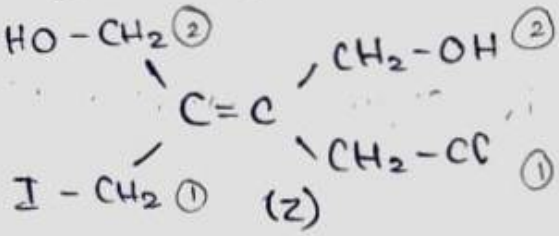


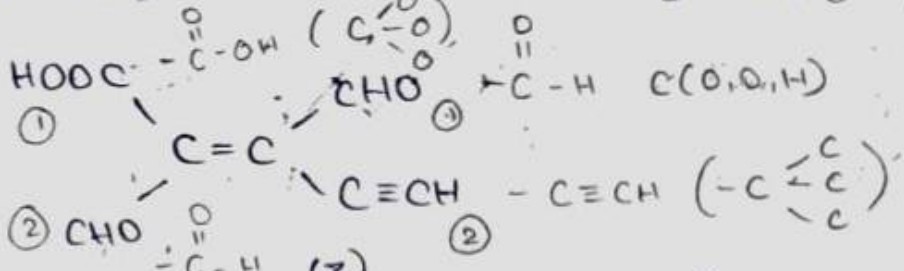


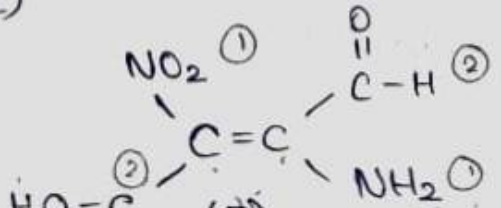




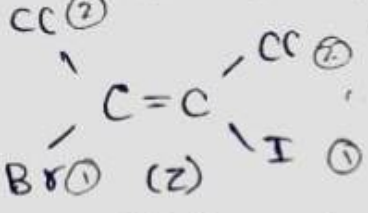


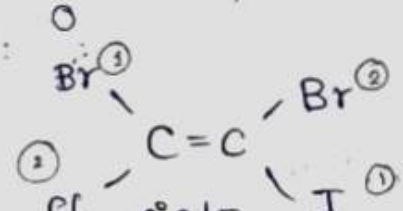






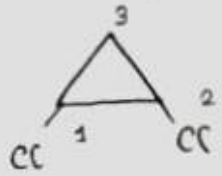
→ More priority for N due to its greater atomic number than C.



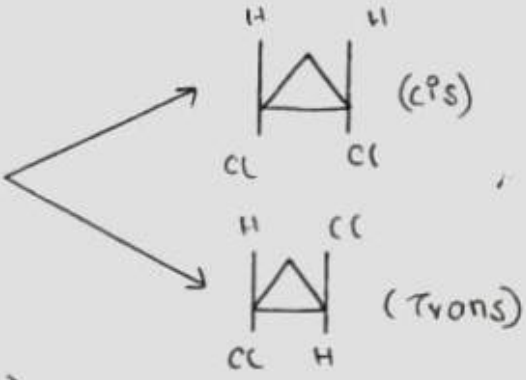


*Note: A cis isomer need not be a Z-isomer.

In cyclo alkanes:

★ 

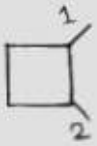
1,2 - dichloro cyclopropane



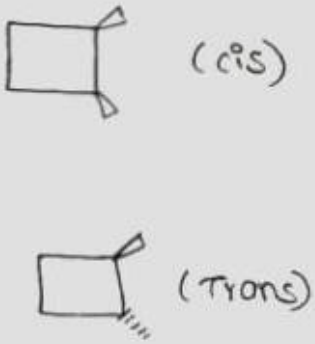
(OR)

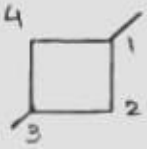
(cis)

(Trans)

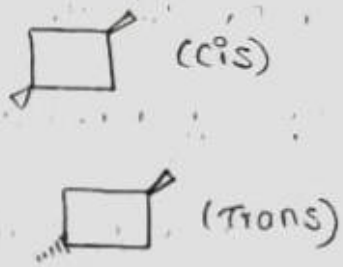
★ 

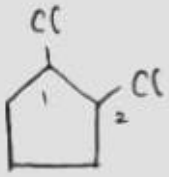
(1,2-dimethyl cyclo Butane)

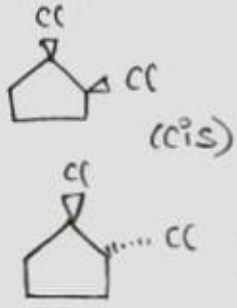


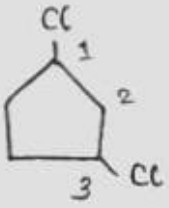
★ 

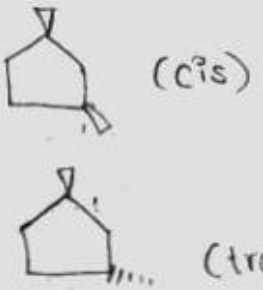
(1,3-dimethyl cyclo Butane)

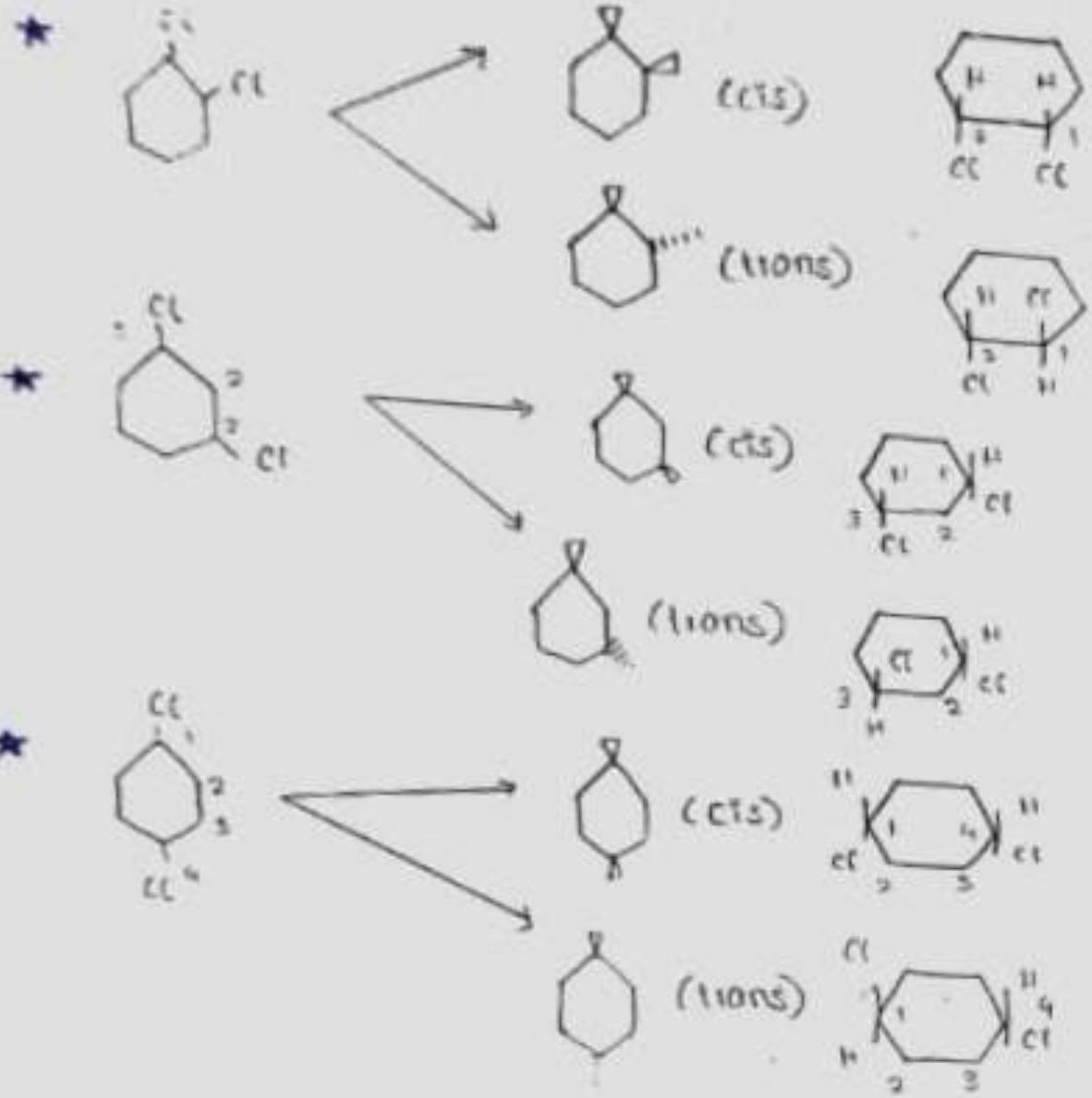


★ 



★ 





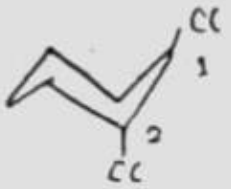
Geometrical Isomerism in chair form of cyclohexane :

Cyclohexane

MF : C_6H_{12}

Position	C-C	trans
(1,2)	(a,e)	(a,a)
	(e,a)	(e,e)

(1,3)	(a,a)	(a,e)
	(e,e)	(e,a)
(1,4)	(a,e)	(a,a)
	(e,a)	(e,e)



Trans 1,2- dichloro cyclo hexane

Cis 1,2- dichloro cyclo hexane

Cis 1,3 dimethyl cyclohexane

Trans 1,3- dimethyl cyclo hexane

Cis 1,3-dimethyl cyclohexane

Trans 1,4- ~~dimethyl~~ dichloro cyclo hexane

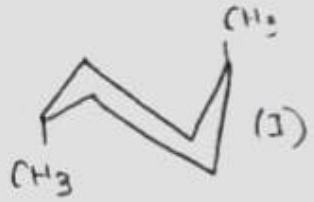
Cis 1,4- dichloro cyclohexane

At equatorial positions, the atoms or groups experience ~~more~~ less repulsion.

Therefore, Axial < Equatorial (Stability)

This can be shown by following example:

Stability:



(I)

Trans, 1-4. dimethyl cyclo hexane

(II)

Trans-1,4-dimethyl cyclo hexane

I < II

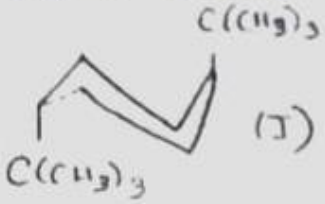
(I)

Cis-1,3-dihydroxy cyclo hexane

(II)

Trans-1,3-dihydroxy cyclo hexane

I > II



(I)

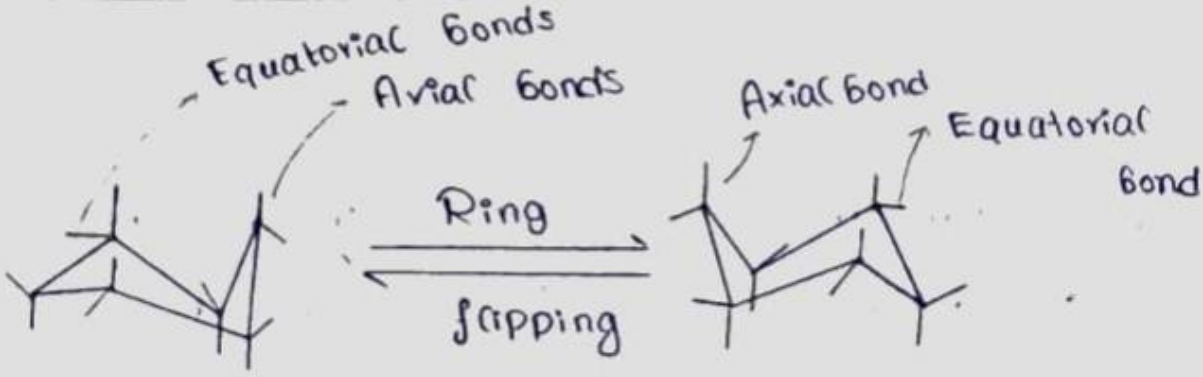
Trans-1,4-di 3° butyl cyclo hexane

(II)

Trans-1,4-di 3° butyl cyclo hexane

I < II

Ring flipping :



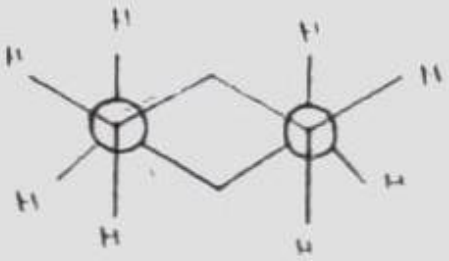
Note : Ring flipping is not possible when one of the alkyl group is isopropyl / 3° butyl. (Bulky groups)

✓ K > 1

$\xrightleftharpoons[\text{flipping}]{\text{Ring}}$ × $K < 1$

$\xrightleftharpoons[\text{flipping}]{\text{Ring}}$ × $K < 1$

Chair form



(staggered)

} → causes torsional strain

(Eclipsed)

G.I. in cyclo alkenes :

Cyclo alkenes can show G.I. when the cyclic ring contains 8 or more than 8 carbon atoms.

(✓)

Cyclo octene (cis)

(✓)

Trans cyclo octene

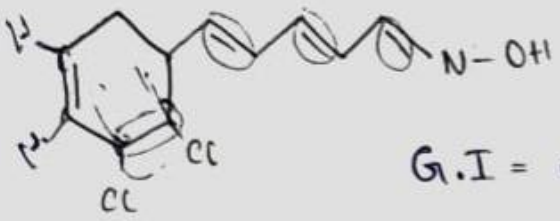
(✓)

Cis, cyclo decene

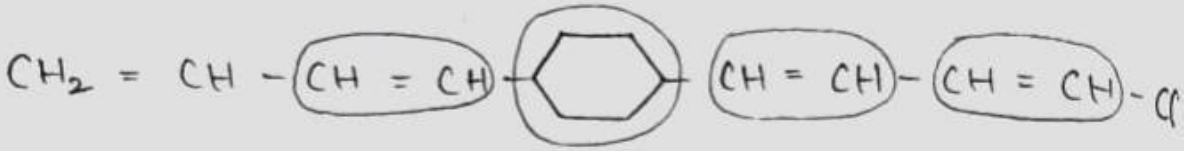
(8 or more than 8 carbon atoms)

(✓)

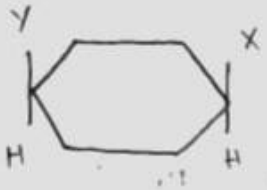
Trans cyclo decene



G.I = $2^n = 2^4 = 16$



G.I = $2^n = 2^4 = 16$



Property	Cis	Trans
Dipolemoment	More	Less/zero
Solubility	More	Less
BP	More	Less
MP	Less	More
Stability	Less	More

*) Geometrical isomers are not mirror image to each other. so they are called diastereomers.

* cis - trans
  syn - onti
  E - Z
  } → Diastereomers

Q) The dihedral angle in staggered form of Newman projection of 1,1,1-trichloro ethane is $15X^\circ$. Then value of x is

$x = 4^\circ$

Q) No. of cis-trans isomers possible for the compound

$2^n = 2^1 = 2$

Q) Identify the compounds in which Gauche conformer is more stable than staggered.

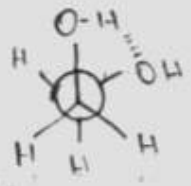
a) 1,2-difluoro ethane

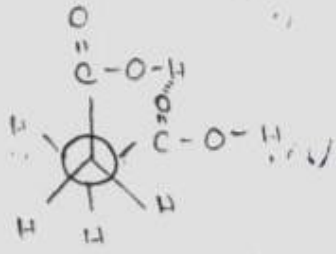
b) Ethylene glycol

c) Succinic acid

d) N-butane

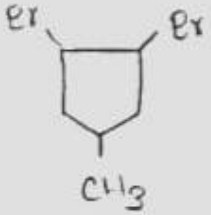
a)

b) 

c) 

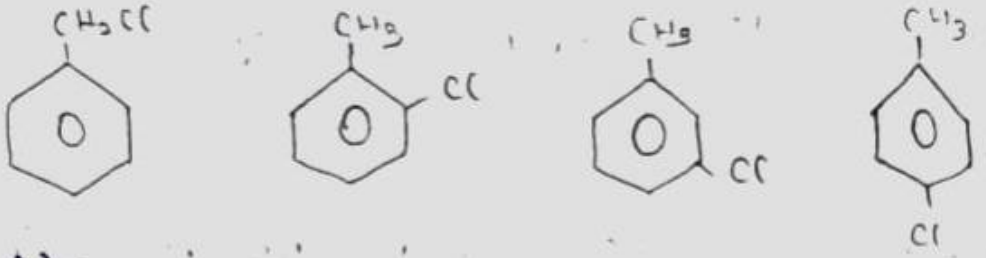
~~Incorrect statement~~

Q) How many G.I are possible



(3)

Q) An aromatic compound of MF C_7H_7Cl has x isomers. Value of x is



$C_4H_{11}N$:

$CH_3-CH_2-CH_2-CH_2-NH_2$

$CH_3-CH(CH_3)-CH_2-NH_2$

1° $CH_3-C(CH_3)_2-NH_2$

$CH_3-CH_2-CH(NH_2)-CH_3$

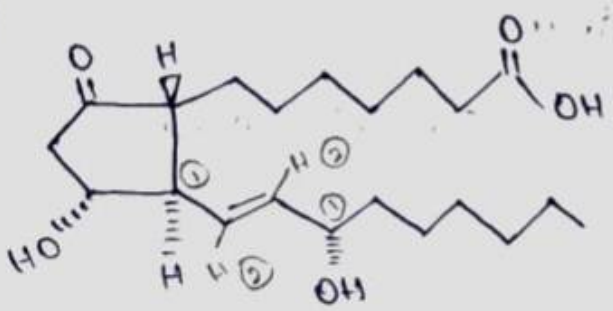
$CH_3-NH-CH_2-CH_2-CH_3$

2° $CH_3-NH-CH(CH_3)_2$

$CH_3CH_2-NH-CH_2CH_3$

$CH_3-N(CH_3)-CH_2-CH_3$ 3°

Q)



What is geometric configuration about the double bond in compound ~~Entagen~~

Answer: E-configuration

Q) $C_5H_{11}Br$

i) $CH_3-CH_2-CH_2-CH_2-CH_2-Br$ ✓

ii) $CH_3-CH(CH_3)-CH_2-CH_2-Br$ ✓

iii) $CH_3-CH_2-CH_2-\underset{\underset{Br}{|}}{CH}-CH_3$ ✓

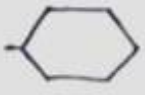
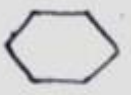
iv) $CH_3-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-Br$ ✓

v) $CH_3-CH_2-\underset{\underset{Br}{|}}{CH}-CH_2-CH_3$ ✓

~~vi~~ vi) $CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-Br$ ✓ (8)

~~$CH_3-CH-CH(CH_3)_2$ (Br)~~ ~~vii~~ viii) $CH_3-\overset{\overset{CH_2-CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Br$ ✓

vii) $CH_3-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_2-Br$ ✓

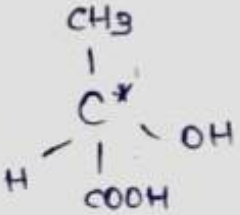
i) Ph-S(=O)(=O)-O-  &  -S(=O)(=O)-O-Ph

Metamers

Optical isomerism:

Chiral carbon (or) asymmetric carbon:

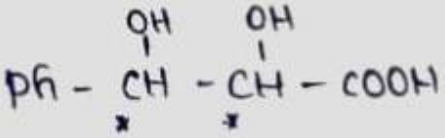
Carbon attached to four different atoms or groups.

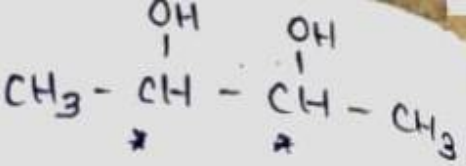
(i) 

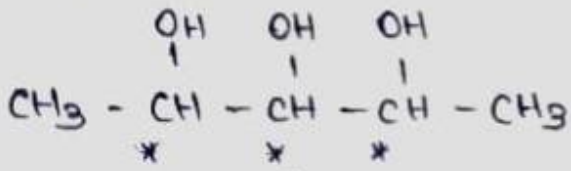
(ii) $CH_3-\overset{*}{C}H(OH)-COOH$ (Lactic acid)

(iii) Ph-$\overset{*}{C}$H(OH)-COOH

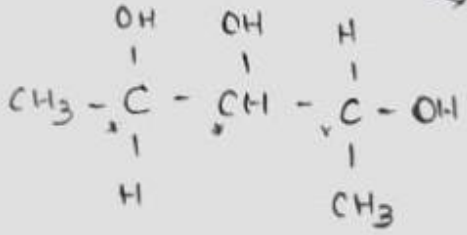
(iv) $CH_3-\overset{*}{C}H(NH_2)-COOH$

(v) 

(vi) 

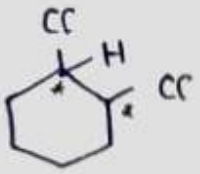
(vii) 

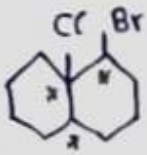
→ Pseudo chiral carbon

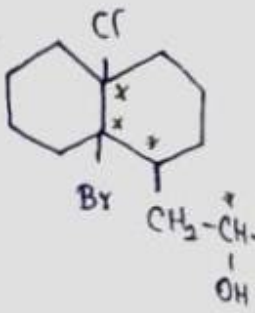


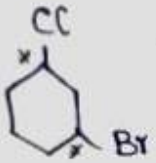
(viii)

No chiral carbon

(ix) 

(x) 

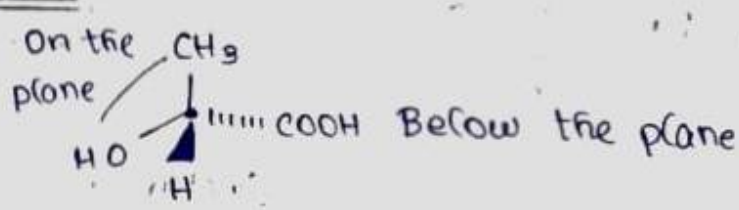
(xi) 

(xii) 

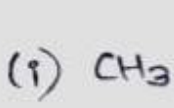
Representation of chiral carbon :

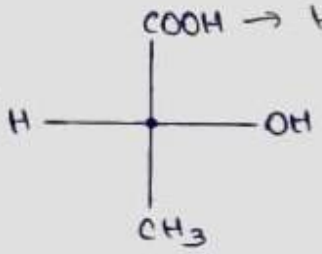
Wedge - dash form :

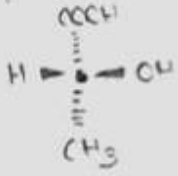
(Lactic acid)

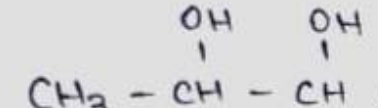


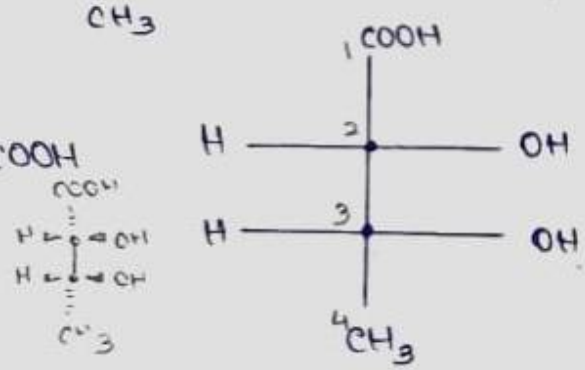
Fischer projection form (2D) :

(i) 

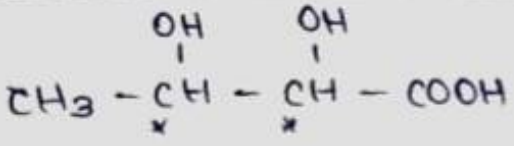


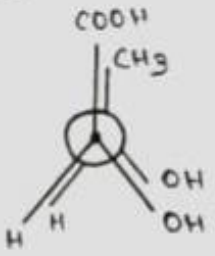


(ii) 

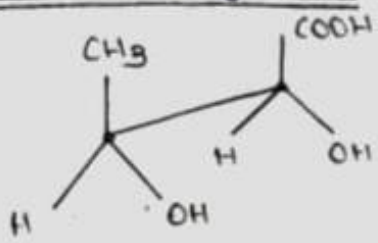


Newman projection form:





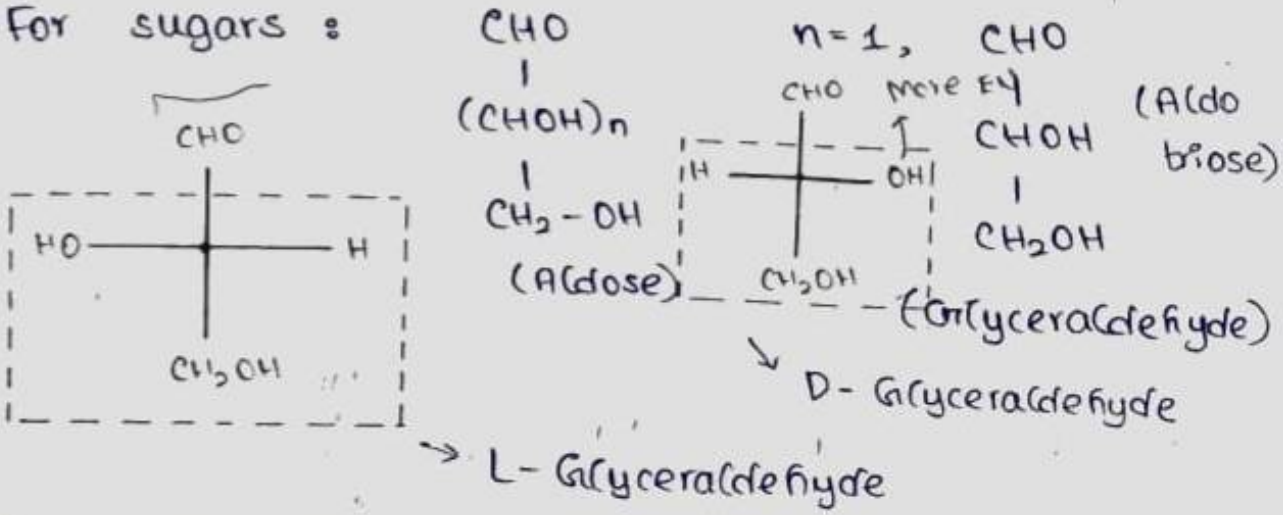
Saw horse form:



Nomenclature of chiral carbon:

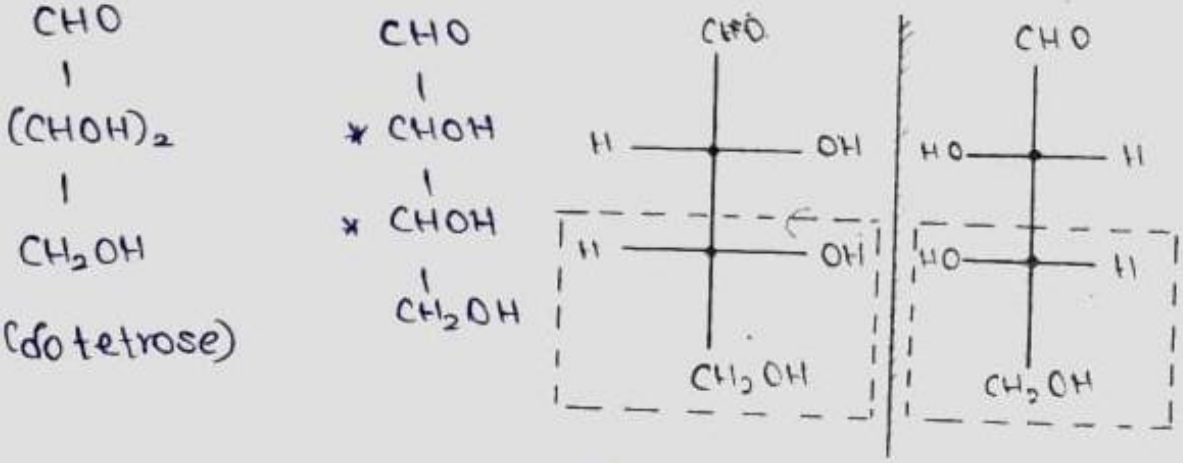
1) D, L - nomenclature (Relative configuration)

For sugars :

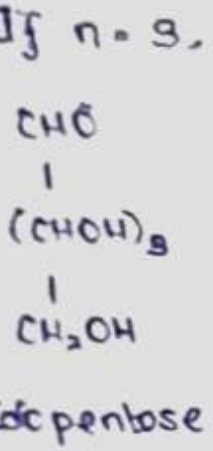


Both are mirror images to each other

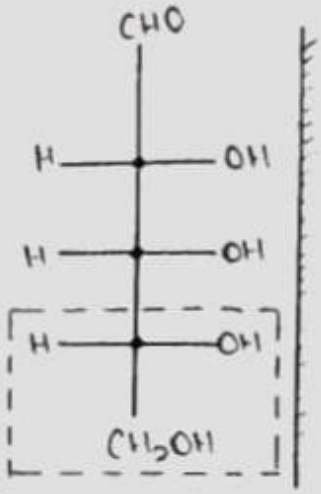
If n = 2,



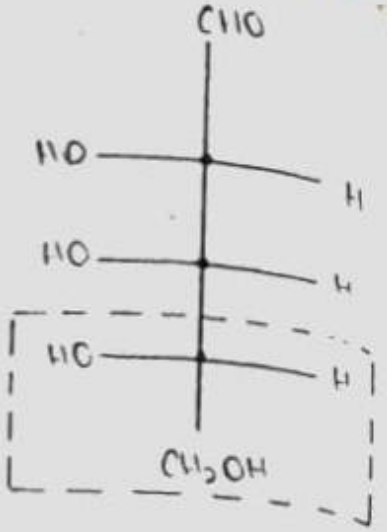
If n = 3,



Aldopentose



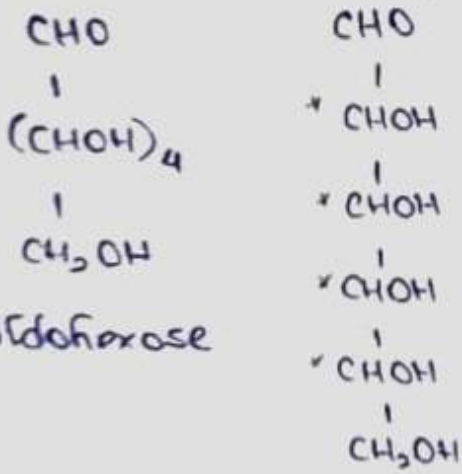
D- ~~Arabinose~~



L- ~~Arabinose~~

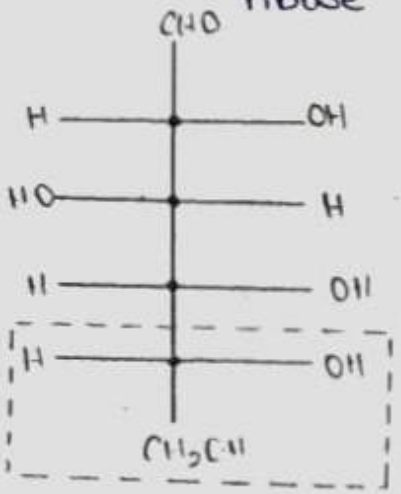
If n = 4,

(Glucose)

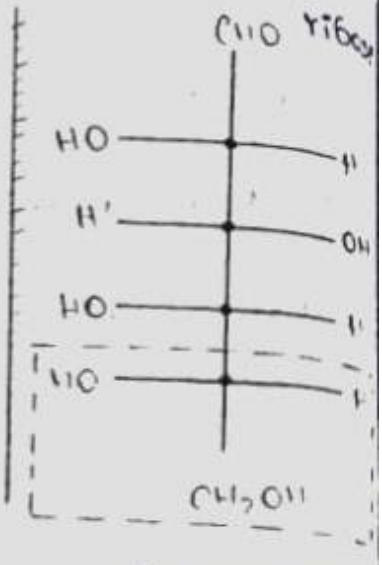


Aldohexose

ribose



D- glucose



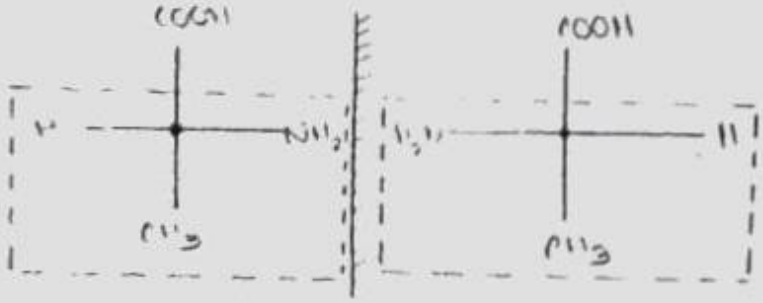
L- glucose

Amino acids :

GF : $R-\overset{*}{C}H-COOH$ (with NH_2 on the starred carbon)

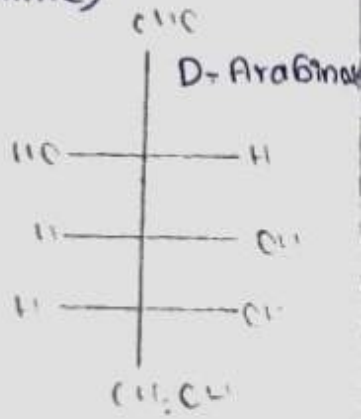
Eg : $CH_3-\overset{*}{C}H(NH_2)-COOH$

(Alanine)



D- Alanine

L- Alanine



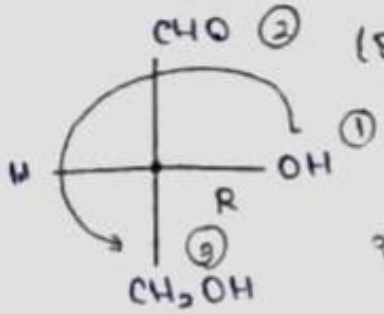
D- Arabinose

R,S - Nomenclature (Absolute configuration) :

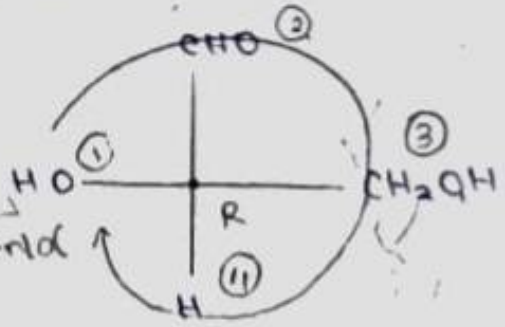
R - Rectus - Right - clockwise

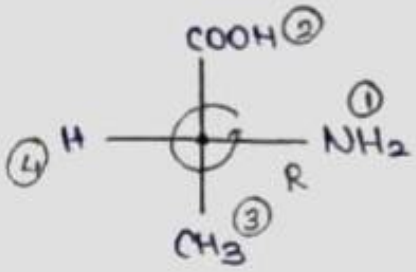
S - Sinster - Left - Anticlockwise

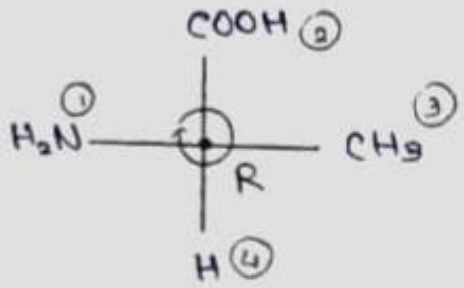
CIP Rules : (Cohn - Ingold - Prelog rules)

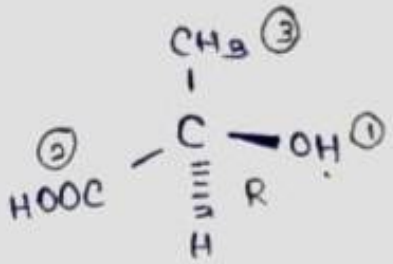


(But least priority group is in horizontal line)





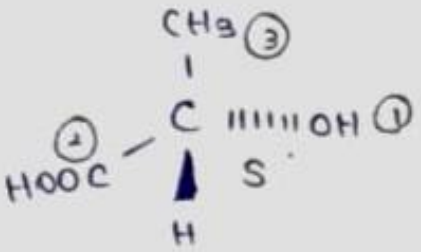




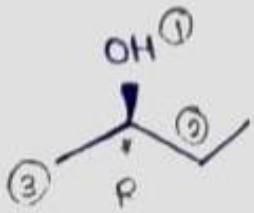
Highest priority atom (Thick)

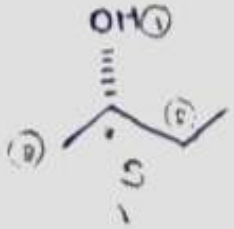
Least priority atom (Dotted)

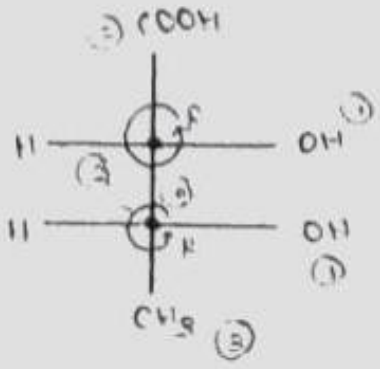
(As it is configuration)

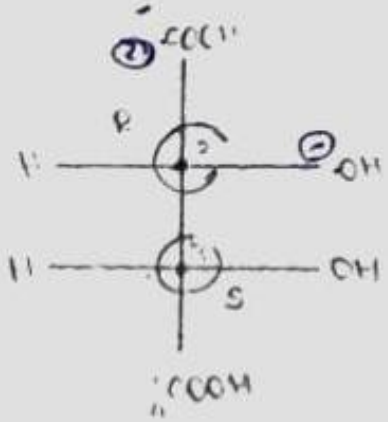


(Because the priority rule is not followed)

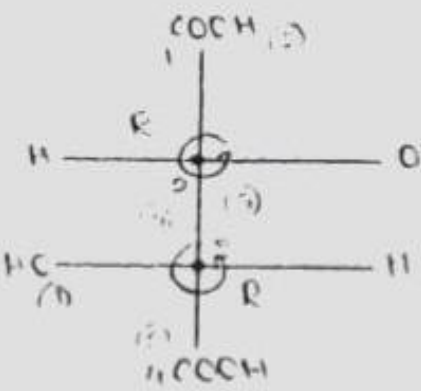




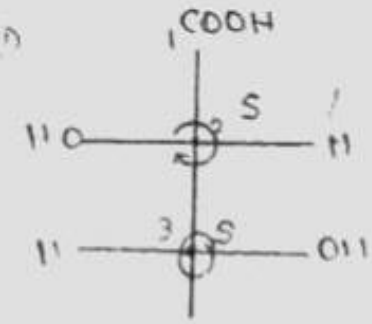




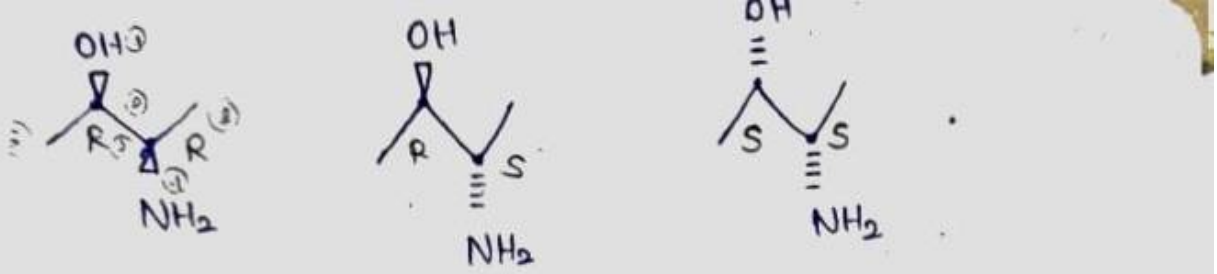
(2R, 3S)



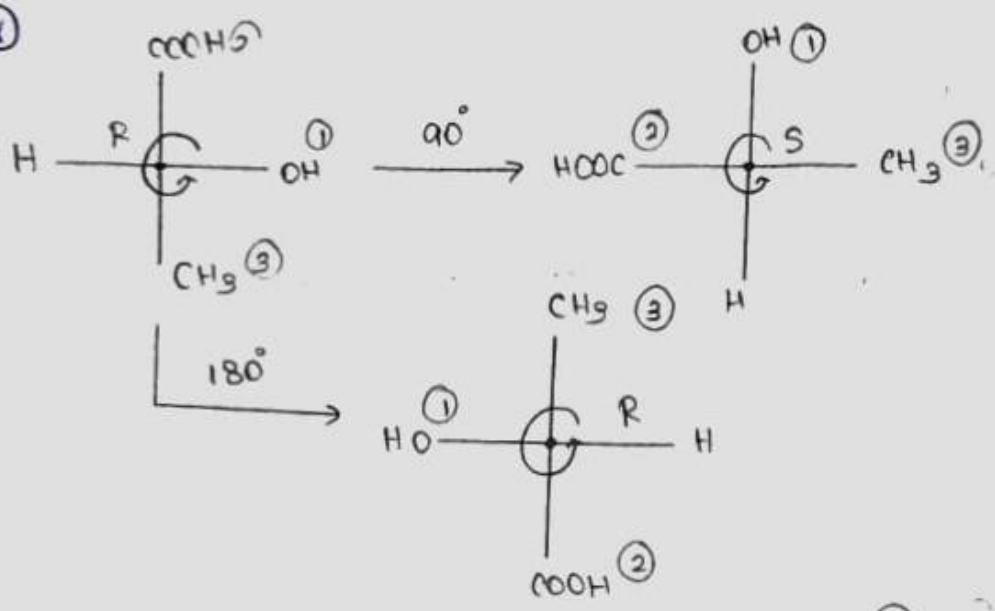
(2R, 3R)

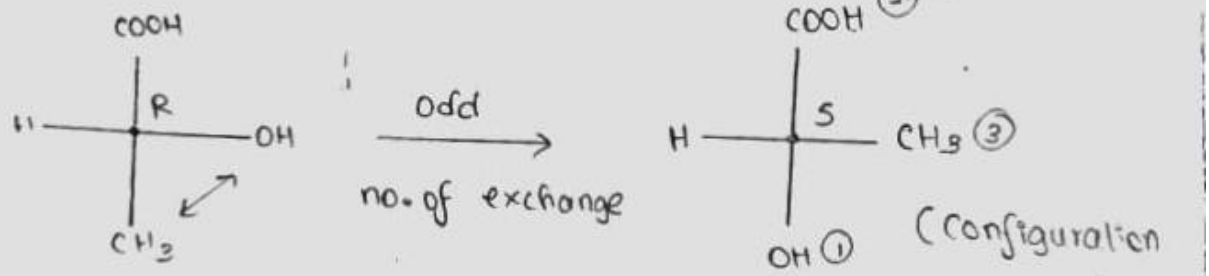


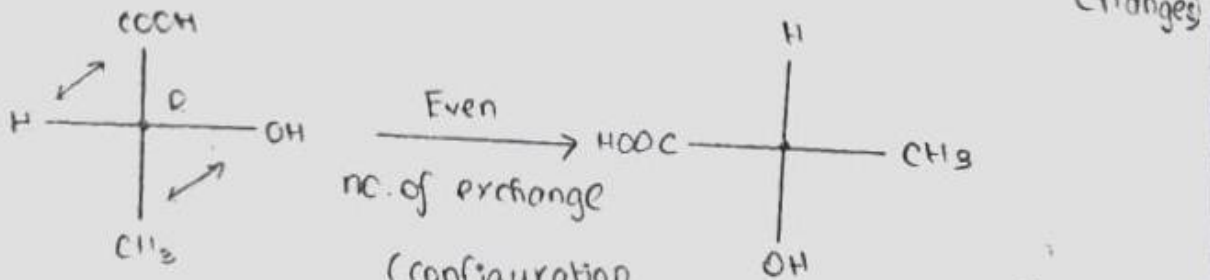
(2S, 3S)

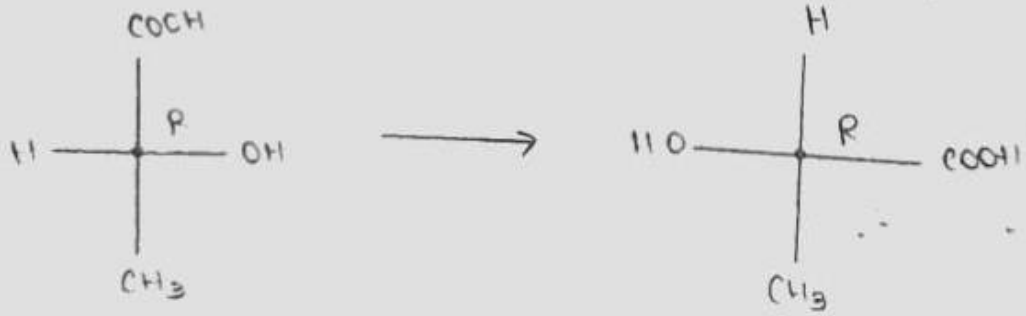


(*)







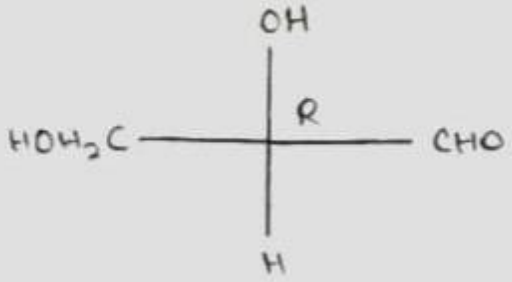


Homomers:

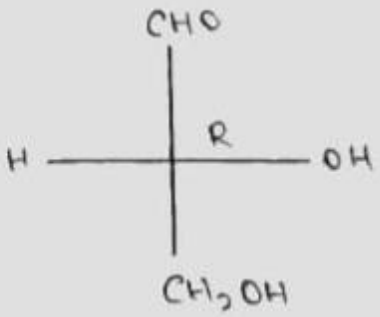
Isomers having same configuration are called as homomers.

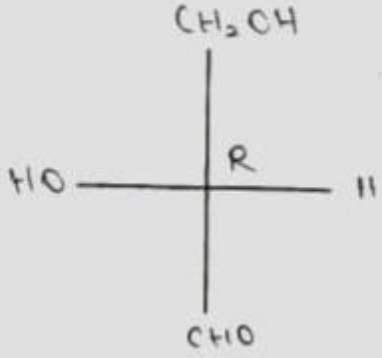
Eg:

1)



2)



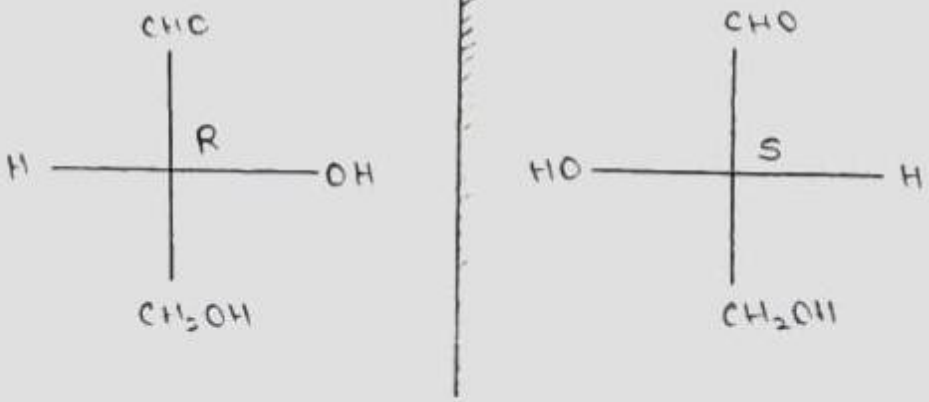


Enantiomers:

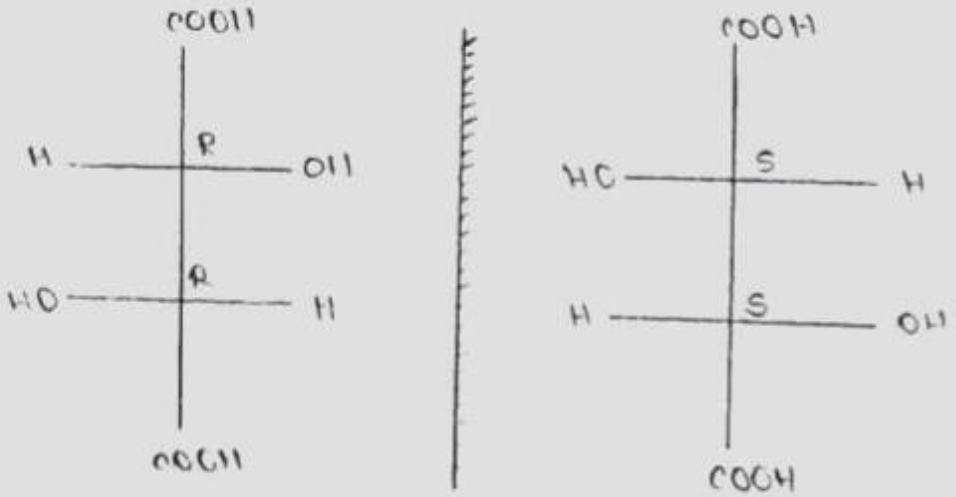
Isomers which are non-superimposable and mirror image to each other are called as enantiomers.

Eg:

1)



2)



3)

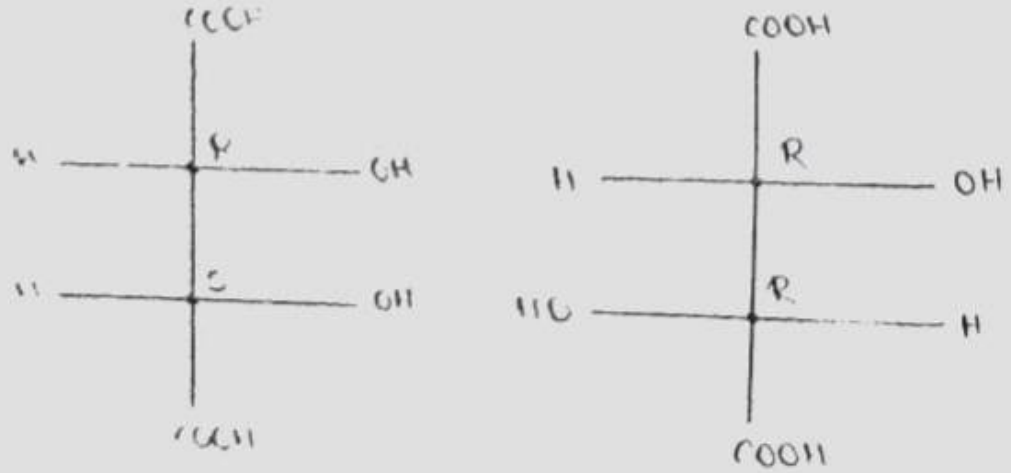
Enantiomeric pair

Enantiomers have some chemical properties and some physical properties like MP, BP, solubility and density, so they can't be seperated by fractional distillation or fractional crystallisation.

Diastereomers:

Stereo isomers which are non-superimposable and non mirror image to each other are called as diastereomers. To form them, compound must contain min. 2 chiral carbons

Eg:

i) 

ii)

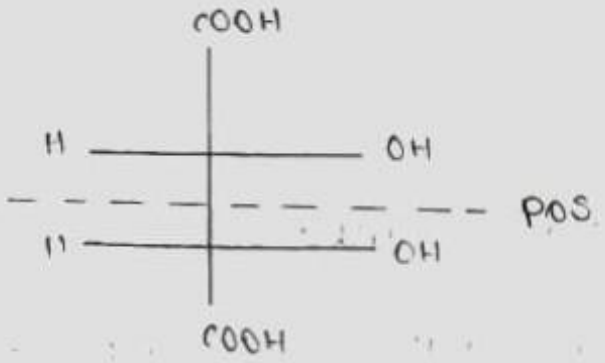
R,R $\xrightarrow{E}$ S,S ; R,S $\xrightarrow{E}$ S,R

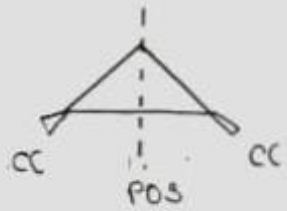
They have same chemical properties but different physical properties (like MP, BP, solubility & density, so they can be seperated by fractional distillation or fractional crystallisation.

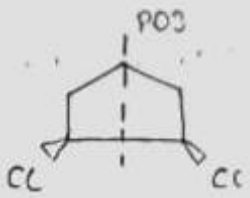
Elements of symmetry:

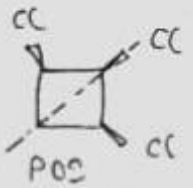
1) Plane of symmetry (POS):

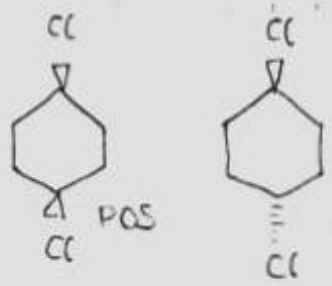
A plane which bisects the molecule into 2 equal halves and which are mirror image to each other called as POS.

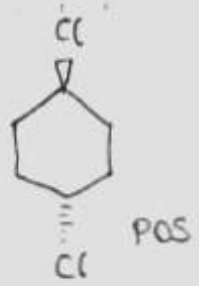


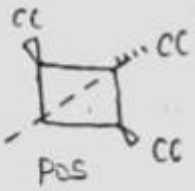


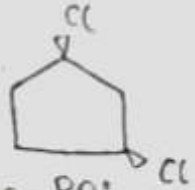


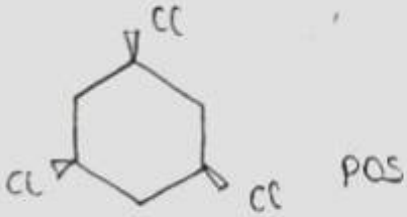








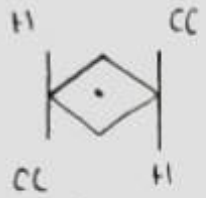




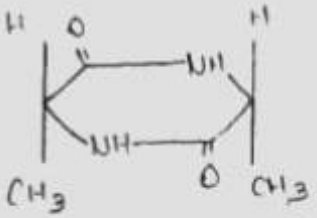
ii) Centre of symmetry (COS):

A line is passing through center of molecule if it meets 2 identical atoms or groups at equal distance then it is said to be having centre of symmetry.

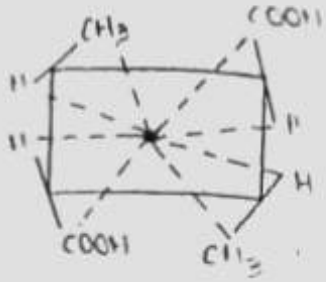
Eg:

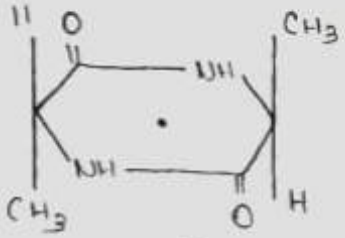


(COS)



(NO COS)





(COS)

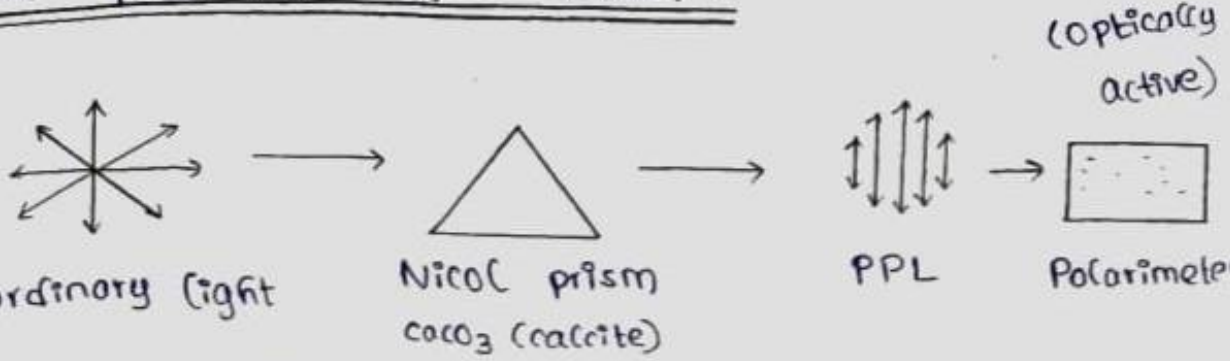
iii) Axis of symmetry:

If a molecule is rotated WRT an axis by 360°, if same appearance is repeated "more than 1 time" then it is said to be having axis of symmetry.

iv) Alternating axis of symmetry:

If a molecule is rotated by 90°, if its mirror image is obtained then it is said to be having alternating axis of symmetry. It is very rare in molecules.

Plane polarised light (PPL):



When an ordinary light is passed through nicol prism (made up of calcite) then all photons of light are vibrated in only one direction or one plane which is called as plane polarised light.

Dextro rotatory compound : (d/(+))/R

Dextro rotatory
clockwise

$\theta = +x^\circ$

When PPL is passed through polarimeter tube which is filled with solution of organic compound, if PPL is rotated in clock wise direction, then it is called as dextro rotatory compound.

Laevo rotatory compound : (l/(-))/S

If PPL is rotated in anti clockwise direction, then it is called as laevo rotatory compound.

Laevo rotatory
anticlockwise

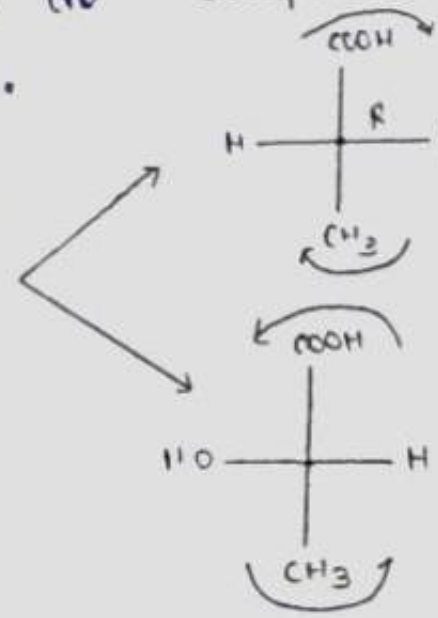
$\theta = -x^\circ$

The necessary condition for optical isomerism is, the compound must be optically active.

Eg:

i) $CH_3 - \underset{OH}{\underset{|}{CH}} - COOH$

Lactic acid



θ = + 3.52°
D- Lactic acid / d- Lactic acid / (+)-Lactic acid

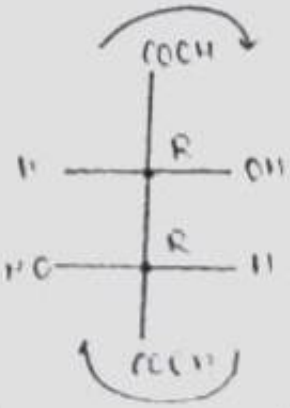
θ = - 3.52°
S- Lactic acid / L- Lactic acid / (-)- Lactic acid

ii) Tartaric acid

$HOOC - \underset{OH}{\underset{|}{CH}} - \underset{OH}{\underset{|}{CH}} - COOH$

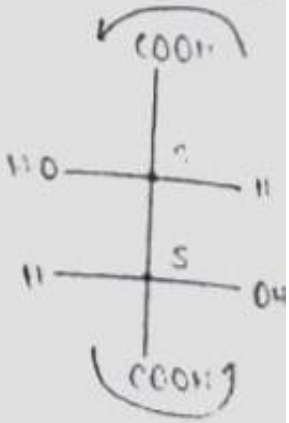
Meso tartaric acid

(optically inactive)



d tartaric acid / (+) tartaric acid / D tartaric acid

(optically active)



L tartaric acid / (-) tartaric acid / S tartaric acid

(optically active)

Meso compound is optically inactive due to internal compensation and because of plane of symmetry.

Racemic mixture:

Equimolar amounts of dextro and laevo forms

called as racemic mixture.

Enantiomeric pair / Racemic mixture is optically inactive due to external compensation But individual compounds are optically active.

Enantiomeric Excess (EE) / optical purity :

$$\% EE = \frac{d-l}{d+l} \times 100$$

$$= \frac{R-S}{R+S} \times 100$$

$$= \frac{n_1 - n_2}{n_1 + n_2} \times 100$$

$$= \frac{w_1 - w_2}{w_1 + w_2} \times 100$$

(If d-form is in excess, it is called pure enantiomer and vice versa).

(n_1 – no. of moles of enantiomer in excess)

Note : Angle of rotation "θ" depends on

i) nature of substance

ii) concentration of solution

iii) temperature

iv) Length of liquid column in polarimeter tube

v) Wave length of light used

vi) specific angle of rotation $(\alpha)_\lambda^T = \frac{\theta}{l \times c}$

where θ is angle of rotation, l is length of liquid column (dm) [1 dm = 10 cm], c is concentration of solution (g/mc).

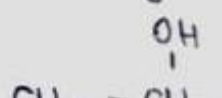
Specific angle of rotation is independent of length and concentration of solution.

Optical isomers:

Isomers having same physical and chemical properties but different only rotation of PPL are called as optical isomers.

Calculation of optical isomers:

① Having unsymmetrical ends with even / odd no. of stereogenic centres:



(lactic acid)

O.I = 2^n [n - no. of stereogenic centres]

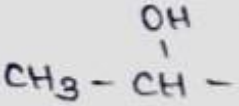
→ active forms ⇒ 2^1 ⇒ 2

O.I = a + m → unsymmetrical ends - No meso compound

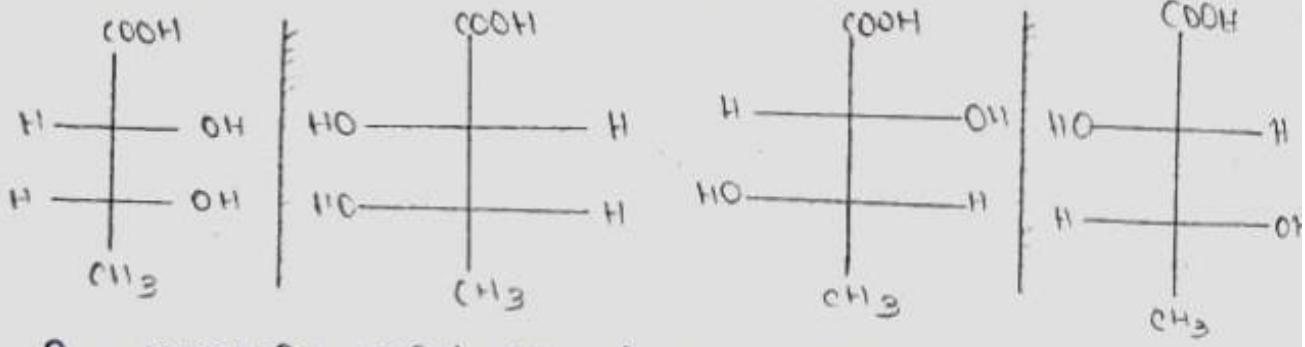
= $2^n + 0$ = 2^n = 2^1 ⇒ 2

i) d-lactic acid (active) ii) l-lactic acid (active)

②



O.I = a + m ⇒ $2^n + 0$ ⇒ 2^2 = 4



2 - racemic mixtures & 2 - enantiomeric pairs

③ $CH_3 - \underset{\overset{|}{Cl}}{\overset{*}{CH}} - \underset{\overset{|}{Cl}}{\overset{*}{CH}} - \underset{\overset{|}{Cl}}{\overset{*}{CH}} - COOH$

$O.I = a + m = 2^n + 0 \Rightarrow 2^3 \Rightarrow 8$

④ Having similar ends

i) If n is even,

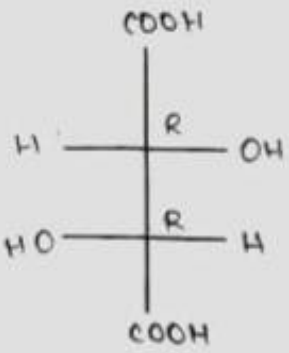
$HOOC - \overset{*}{\underset{\overset{|}{OH}}{CH}} - \overset{*}{\underset{\overset{|}{OH}}{CH}} - COOH$ (n-2)

(Tartaric acid)

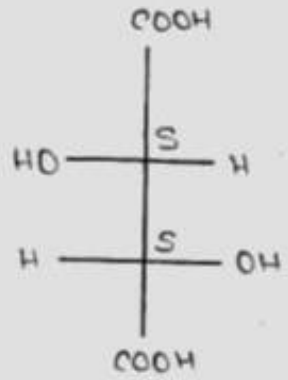
$O.I = a + m$

$= 2^{n-1} + 2^{n/2-1}$

$= 2^1 + 2^{1-1} \Rightarrow 3$

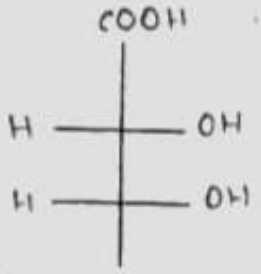


δ- tartaric acid



L- tartaric acid

→ Active forms



Meso tartaric acid ← (optically inactive)

ii) If n is odd,

$HOOC - \overset{OH}{\overset{|}{CH}} - \overset{OH}{\overset{|}{CH}} - \overset{OH}{\overset{|}{CH}} - COOH$ (n=3)

↓

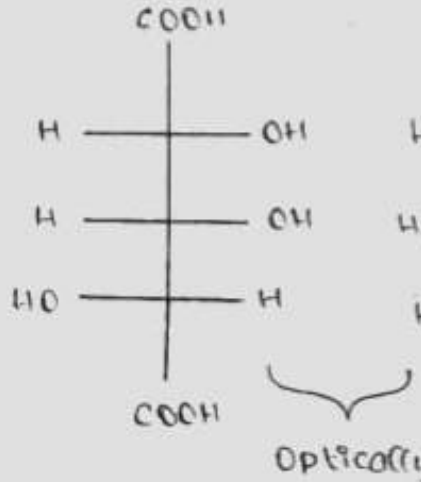
Pseudo chiral carbon

$O.I = a + m$

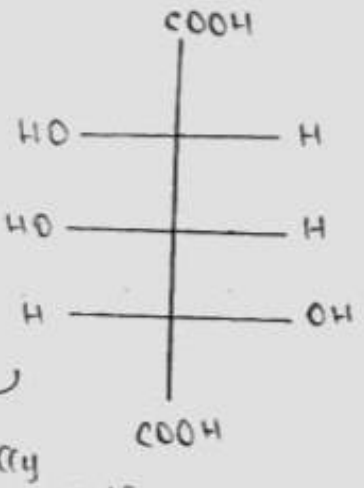
$= (2^{n-1} - 2^{\frac{n-1}{2}}) + 2^{\frac{n-1}{2}}$

$a = 2^{n-1} - 2^{\frac{n-1}{2}} \Rightarrow 2^2 - 2^1 \Rightarrow 2$

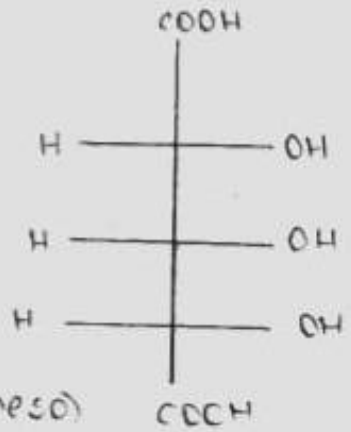
$m = 2^{\frac{2}{2}} = 2$



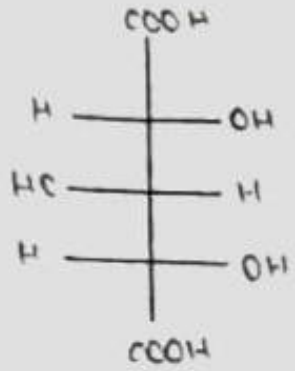
Optically active



They are enantiomers



(Meso) Inactive



(Meso)

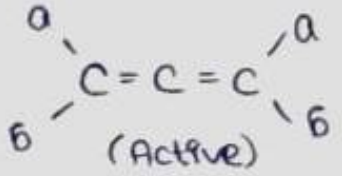
Inactive

Optical isomerism in disymmetric molecules:

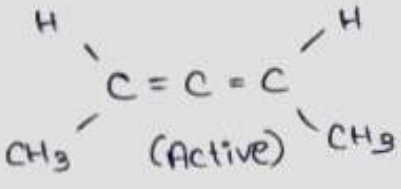
Disymmetric molecules are optically active because they don't contain symmetry (POS & COS). Disymmetric molecules do not contain chiral carbon, even though they are active.

Example:

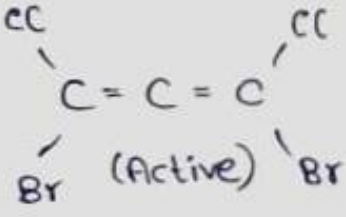
1) Allene derivatives:



(Active)

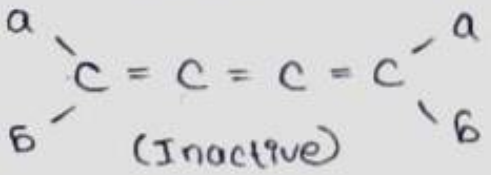


(Active)



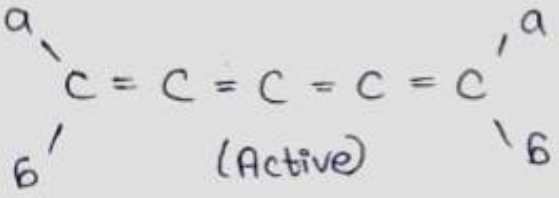
(Active)

2) In cummulated polyenes:



(Inactive)

Geometrical isomerism is exhibited by this compound



(Active)

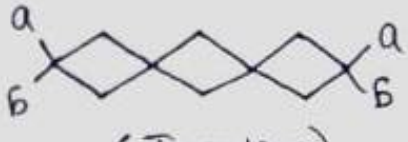
No symmetry (2O.I) cannot exhibit G.I.

3) In spiro compounds:

(Active)

G.I. (X)

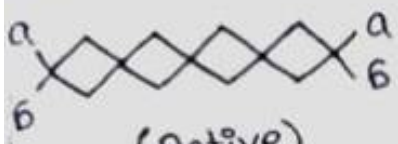
O.I. (√)



(Inactive)

G.I. (√)

O.I. (X)

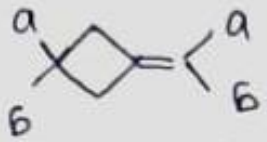


(Active)

G.I. (x)

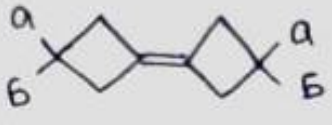
O.I. (√)

4) In cyclo alkylidenes :



(Active)

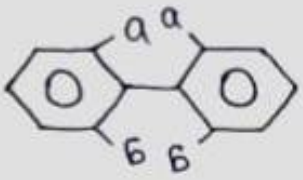
(G.I) √ (O.I) √



(Active)

(G.I) √ (O.I) √

5) In Biphenyls :



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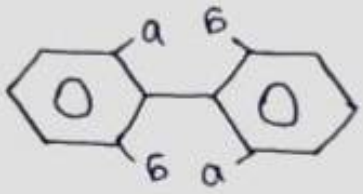

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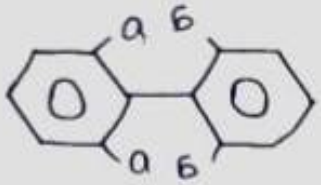

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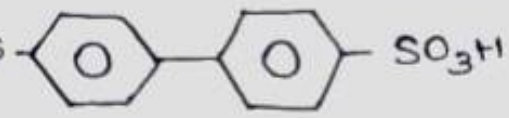

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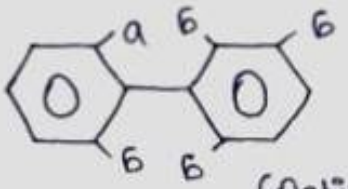
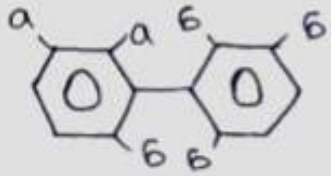


(Active)



(Active)

Chiral carbon

(or)

Asymmetric carbon

(Optically active)

No chiral carbon

Disymmetrical molecule

(optically active)

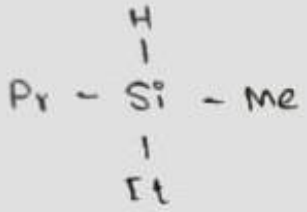
chiral molecule

The necessary condition for optical isomerism is compound must be disymmetric i.e., it should not contain symmetry.

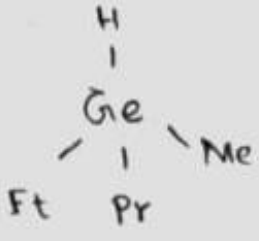
All asymmetric molecules are disymmetric but not vice versa.

Eg:

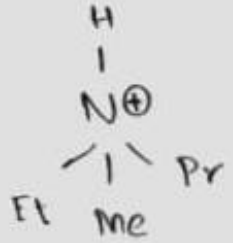
(Active)



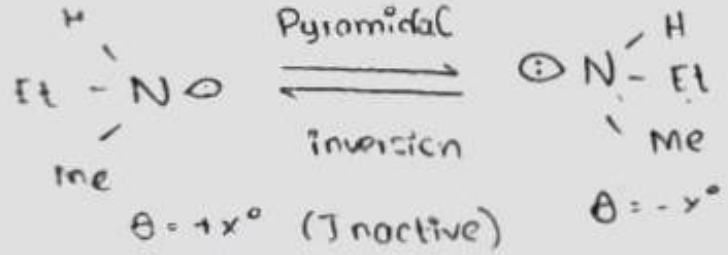
(Active)



(Active)



(Active)



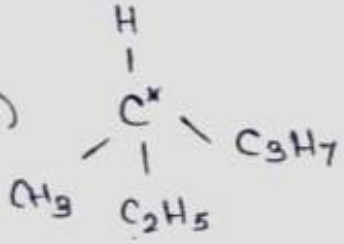
$\theta = +x°$ (Inactive)

$\theta = -x°$

Min. no of carbons required for an alkane to show optical isomerism is 7.

MF: C_7H_{16}

(OR)



Calculation of Stereo isomers (GI + OI):

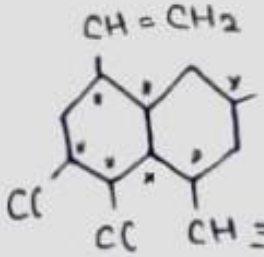
S.I = 2^n n: No. of stereogenic centers

$CH_3 - CH = CH - \underset{*}{CH}(Cl) - CH_3$ n = 2

S.I = $2^n = 2^2 = 4$

$CH_2 - CH = CH - CH = N - OH$

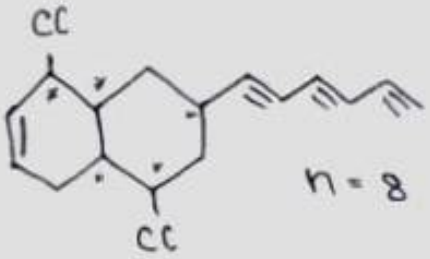
$CH = CH - CH_3$ n = 3 S.I = $2^3 = 8$



$CH \equiv CH - N \equiv N - CH \equiv N - OH$

$n = 11$

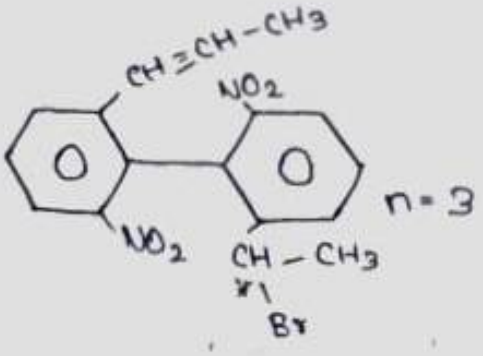
$S.I = 2^n = 2^{11}$



$n = 8$ $\quad S.I = 2^8$

$n = 2$

$S.I = 2^2 = 4$



$n = 3$

$S.I = 2^3 = 8$

For bridged compounds, we should consider only one stereogenic center.

) $CH_3 - \underset{2}{CH}(CH_3) - CH_2 - CH_3 \xrightarrow[\text{Mono chlorination}]{Cl_2/h\nu}$

2-methyl Butane

(Isopentane)

$CH_2Cl - \underset{*}{CH}(CH_3) - CH_2 - CH_3 \quad (2)$ (Active)

+

$CH_3 - \underset{Cl}{C}(CH_3) - CH_2 - CH_3 \quad (1)$ (Inactive)

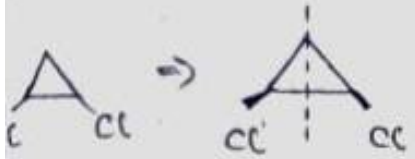
+

$CH_3 - \underset{Cl}{\underset{*}{CH}} - \underset{*}{CH}(CH_3) - CH_3 \quad (2)$ (Active)

+

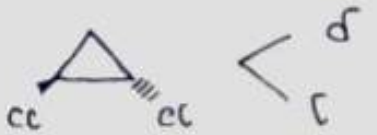
$CH_2Cl - CH_2 - CH(CH_3) - CH_3 \quad (1)$ (Inactive)

*) 1,2-dichloro cyclo propane



cis

(Inactive)



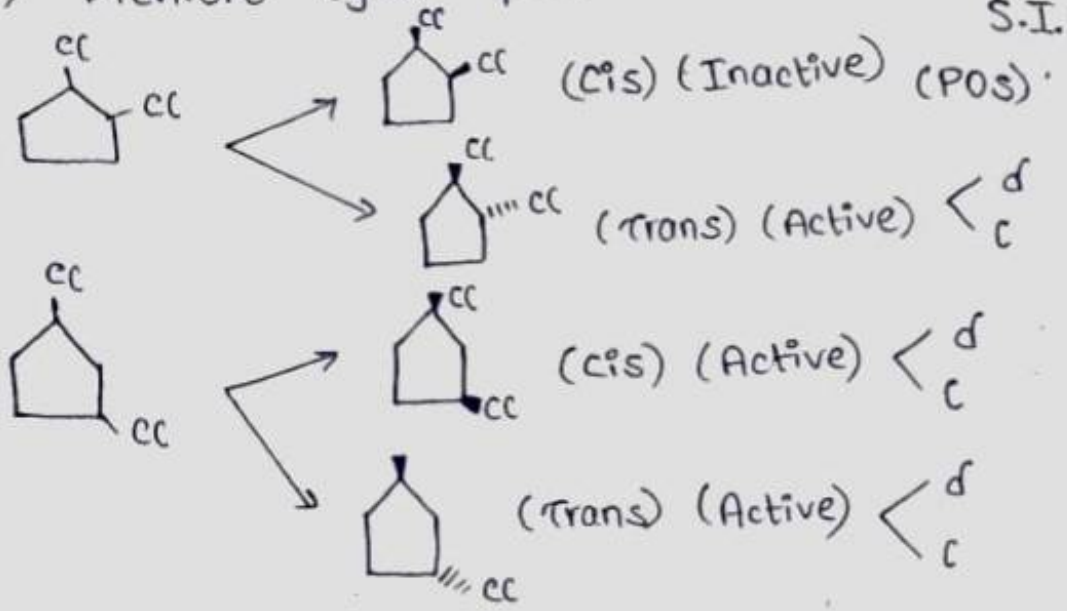
S.I = 3

(Trans)

Active

*) Dichloro cyclo pentane

S.I. = 7



Eg

8) If a mixture of 2-Bromo butane has enantiomeric excess of 50% of (+) 2-Bromo butane. The stereoisomeric composition of the mixture WRT (+) & (-) enantiomers respectively.

Sol:

50% Remaining 50% (RM)

(+) 25% (-) 25%

S.I. composition of (+) = 25 + 50 → 75%

(-) = 25%

Q) A solution is prepared by mixing 10 mL of 0.1 M solution of R-enantiomer & 30 mL of 0.1 M solution of S-enantiomer. Calculate % of Enantiomeric excess.

$M = \frac{n}{V}$; $n = M \times V \Rightarrow 1_{(R)}$ & $3_{(S)}$

$EE\% = \frac{3-1}{3+1} \times 100 \Rightarrow \frac{2}{4} \times 100 \Rightarrow 50\%$

$$\% \text{ EE} = \frac{\text{Observed specific rotation}}{\text{Specific rotation of pure enantiomer}} \times 100$$

Q) Obs. specific rotation of (+) 2-Butanone is $+13.9^\circ$. A sample of 2-Butanone containing both the enantiomers was found to have a specific rotation value of $(-)\ 3.5^\circ$ under similar condition. Then calculate % of (+) and (-) enantiomers present in the sample.

~~% EE = 13.9 / 3.5~~

$$\% \text{ EE} = \frac{-3.5}{-13.9} \times 100 \approx 25\%$$

Remaining mixture = 75 % (RM)

(+) 37.5 % (-) 37.5 %

(+) form is 37.5

(-) form is 62.5

Resolution :

Seperation of racemic mixture (±) & into individual (+) & (-) forms called as resolution. Only optically active compounds can be resolved.

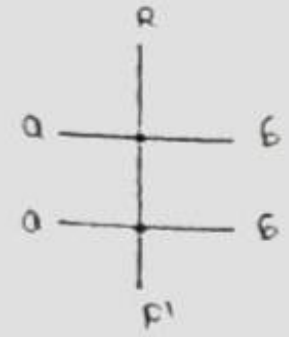
Racemisation :

Conversion of either (+) or (-) form into

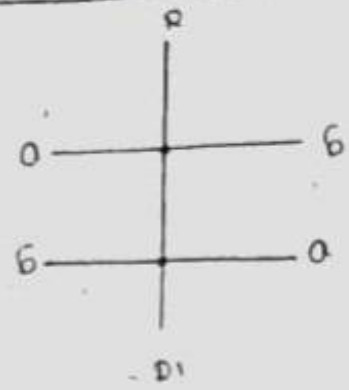
racemic mixture called as racemisation.

Erythro - threo nomenclature :

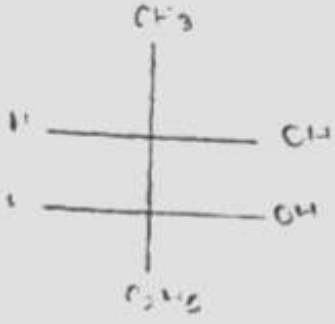
Eg



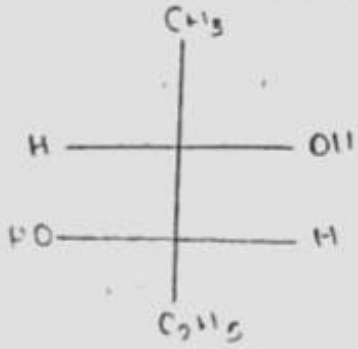
Erythro



Threo



Erythro

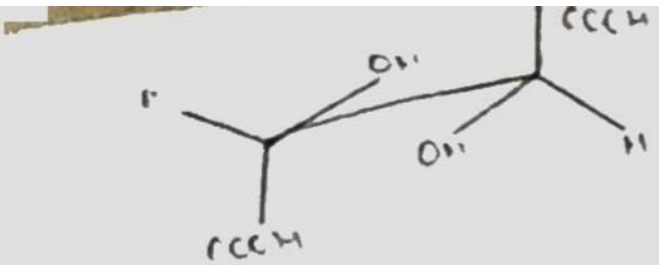


Threo

Fischer - Newman :

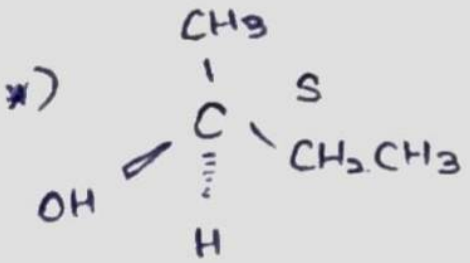
Fischer - sawhorse :

(Eclipsed)



(Staggered)

*)



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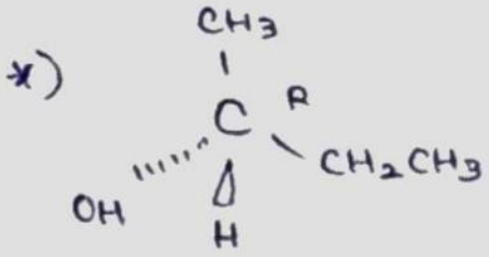

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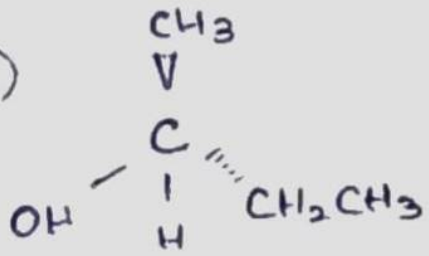

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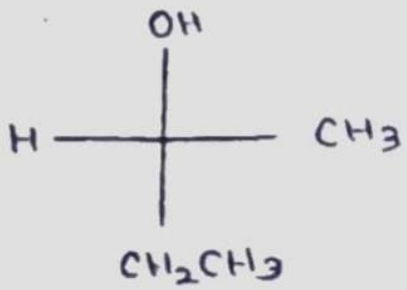

(±) - written at the bottom Remoining are written in clockwise direction.